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# A STUDY OF RESISTIVITY AND CONDITIONING OF FLY ASH

Southern Research Institute

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# A STUDY OF RESISTIVITY AND CONDITIONING OF FLY ASH

Final Report To

ENVIRONMENTAL PROTECTION AGENCY

Office of Air Programs

Contract CPA 70-149

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# ABSTRACT

An experimental study was made of the injection of $SO_3$ or $H_2SO_4$ gaseous conditioning agent to alleviate the problem of high electrical resistivity of fly ash. This problem interferes with the electrostatic precipitation of fly ash in power stations burning low-sulfur coals and thus providing very low concentrations of $H_2SO_4$ as a naturally occurring conditioning agent. Experimental measurements included in the study consisted of determinations of fly-ash resistivity *in situ* and analyses of coal, flue gases, and fly ash with injected $SO_3$ and $H_2SO_4$ concentrations up to 50 ppm. For comparison with conditioning by injected $SO_3$ or $H_2SO_4$, a parallel study was made of conditioning by $H_2SO_4$ as produced naturally during the burning of coal. To compare the economic aspects of different processes of $SO_3$ and $H_2SO_4$ injection, an analysis was made of the various capital and operating costs in existing injection facilities.

Further experimental study was made of the use of $NH_3$ and $H_2O$ conditioning agents. Usually, $NH_3$ is used at low concentrations comparable to those of $SO_3$ or $H_2SO_4$ for the same purpose—that is, to lower electrical resistivity to a desirable range. However, during this investigation, $NH_3$ was studied as a means of coping with poor precipitator efficiency in a power station burning a high-sulfur coal and thus producing an undesirably high concentration of $H_2SO_4$. At customary precipitator temperatures, the $H_2O$ vapor produced during the combustion of coal normally acts in some degree as a naturally occurring conditioning agent, usually at concentrations between 5 and 10% by volume in the flue gases. As part of this investigation, the effect of $H_2O$ injection was observed in one plant with the concentration increased to 14% from the normal value of 7%.

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# SUMMARY

This report summarizes an experimental study that was performed for the Environmental Protection Agency, Office of Air Programs, under Contract CPA 70-149, entitled "A Study of Resistivity and Conditioning of Fly Ash." The study was started in July, 1970, and concluded in August, 1971.

The electrical resistivity of fly ash is one of the most important parameters that controls the efficiency of fly-ash removal in coal-burning power stations by the use of electrostatic precipitators. If the resistivity is too high, as it is normally when a low-sulfur coal is burned, the collection efficiency is poor because the electric field between the corona wires and the collecting electrodes falls to a low value, excessive sparking occurs in the interelectrode space, or back corona occurs in the deposited fly ash. Alternatively, if the resistivity is too low, as it may be when a high-sulfur coal is burned, collection efficiency can again be poor because the electrical force holding deposited ash on the collecting electrodes is not high enough to prevent excessive reentrainment during rapping of the electrodes. The upper limit of the acceptable resistivity range is approximately $2 \times 10^{10}$ ohm cm, and the corresponding lower limit is about $1 \times 10^{7}$ ohm cm. Various gaseous agents—mainly $SO_3$, $H_2SO_4$, $NH_3$, and $H_2O$—can be injected into the stream of flue gases to overcome the problem of high resistivity. One of the agents—$NH_3$—can also be used to cope with the problem of low resistivity.

The initial task in this experimental study was to develop or select apparatus that would be appropriate for making determinations of fly-ash resistivity and flue-gas concentrations. Several devices for in situ measurements of resistivity were fabricated and used in field experiments. A gas sampling train for collecting sulfur oxides was the principal apparatus for gas analysis; it consisted of a condenser for $SO_3$ (always present as $H_2SO_4$ vapor in the customary range of precipitator temperatures) and an aqueous $H_2O_2$ bubbler for $SO_2$.

The central task in the field studies was to evaluate the effects on fly-ash resistivity that are produced by injecting $SO_3$ or $H_2SO_4$ vapor in the flue gases of power stations burning coals with low sulfur contents (approximately 0.5% by weight). Most of these studies were carried out in the Cherokee and Arapahoe plants of the Public Service Company of Colorado, where provision had been made to inject $SO_3$ by the evaporation of the stabilized liquid oxide in dry air or to inject $H_2SO_4$ by the evaporation of the concentrated liquid acid, either at a low temperature in ambient air or at a high temperature in the combustion products

from natural gas. Regardless of the injection system used, the injected agent occurs in the flue gases as $H_2SO_4$, and it acts as a supplement to the low concentration of $H_2SO_4$ produced in the combustion of low-sulfur coal. An additional study was carried out in another power station with a low-sulfur fuel and a low-temperature $H_2SO_4$ injection system; the results obtained by other investigators in still another power station with a low-sulfur coal and an $SO_3$ injection system were made available for comparison with the results of the field studies in this program. Conditioning parameters that varied in the different power stations included the gas temperature; the fly-ash concentration, particle size, and chemical constitution; and the site of $SO_3$ or $H_2SO_4$ injection (upstream from both mechanical and electrostatic collectors, between the two types of collectors, or upstream from an electrostatic precipitator in the absence of a mechanical collector).

All but one of the injection systems produced the desired lowering of the fly-ash resistivity. The one exception was of the high-temperature $H_2SO_4$ type; the ineffectiveness of this system may have been attributable to an inadequate distribution system, and the conclusion that the system is inherently unsound is not warranted by the results obtained in this program. In general, the experimental findings indicated that each of the conditioning parameters enumerated above had some bearing on the injected concentration of $SO_3$ or $H_2SO_4$ that was needed for optimum results. However, the experimental results can be generalized as follows: an injected concentration of 20 ppm was sufficient to produce the desired lowering of resistivity in each instance. To the degree that fly-ash basicity or flue-gas temperature was lowered, the required concentration was lowered. Conclusions about the mechanisms of $H_2SO_4$ conditioning are given later in this summary, inasmuch as they are based in part on data obtained in plants without conditioning facilities, where only naturally occurring $H_2SO_4$ was present.

A study of $NH_3$ conditioning was made in the Widows Creek power station of the Tennessee Valley Authority. The working hypotheses to explain the role of $NH_3$ in this plant were that this basic conditioning agent neutralizes the excessively high concentration of naturally produced $H_2SO_4$ from high-sulfur coal (about 4% sulfur), raises the resistivity of the fly ash, and minimizes reentrainment losses in the precipitator. From the results obtained in this program, none of these hypotheses can be unequivocally disputed. However, in repeated experiments, the expected raising of resistivity was not observed, and this hypothesis seems at present to be erroneous. If it is erroneous, the mechanism by which $NH_3$ increases the precipitator efficiency must be different in some respects from that described. Under a future research program, further efforts will be made to explain the role of $NH_3$ at the Widows Creek plant.

A very brief study of $H_2O$ conditioning was made at the Kingston station in the TVA system. It was found that with 2% sulfur as the fuel, the flue gases contained about 10 ppm of $H_2SO_4$ and 7% of $H_2O$ as vapors at the temperature investigated, about 330°F, but the fly-ash resistivity was higher than desired under these conditions. Subsequently, however, it was found that injecting a stream of water into the boiler to increase the concentration of $H_2O$ vapor to 15% gave an appreciable reduction in resistivity and, simultaneously, a decrease in the concentration of $H_2SO_4$ to 3 ppm and a corresponding increase in the sulfate content of the fly ash. These results illustrate one of the tenets reached in explaining the mechanism of $H_2SO_4$ conditioning: $H_2SO_4$ and $H_2O$ vapors act in conjunction to control the resistivity of fly ash.

Among the studies made in plants without conditioning facilities, the results obtained at the Shawnee plant of the TVA system were among the most meaningful data. Tests were performed with and without injection of dry limestone into the boiler as a means of controlling the emission of $SO_2$. The highly basic particles of lime formed during the calcining of the limestone virtually eliminated the naturally produced $H_2SO_4$ from the flue gases and produced a mixture of lime and fly-ash particles with a resistivity much above the level considered practical for efficient precipitator operation.

One of the final tasks in this program was to explain the mechanism of fly-ash conditioning with $H_2SO_4$ and to establish certain guidelines as to the expected efficiency of conditioning with a variation in the parameters considered relevant. The following conclusions were reached:

- $H_2SO_4$ and $H_2O$ vapors are concurrently collected on the surface of fly-ash particles, producing a low-resistance path for the flow of electricity on the surface rather than through the interior of the particles.

- Joint collection of $H_2SO_4$ and $H_2O$ vapors can occur by the mechanism of adsorption at temperatures above the dew point of the mixture of vapors. Clearcut evidence to support this conclusion was obtained in one of the plants with a flue-gas temperature unequivocally above the dew point. Unequivocal evidence pertinent to this conclusion could not generally be obtained in the other power stations with lower temperatures because of the present uncertainty about the exact location of the dew point at specified $H_2SO_4$ and $H_2O$ concentrations.

- Joint collection of $H_2SO_4$ and $H_2O$ by condensation undoubtedly will occur at sufficiently high vapor concentrations and low temperatures. Thus, condensation is a possible mechanism of conditioning, but it is not a necessary mechanism.

- Low temperature or low fly-ash basicity favor conditioning by a given concentration of $H_2SO_4$. It appears that a surface layer containing $H_2SO_4$ *per se* is essential for effective conditioning. If the fly ash is chemically neutral, such a layer is readily produced. On the contrary, if the fly ash is markedly basic, as it is with a high lime content, the $H_2SO_4$-containing layer is less readily produced, owing to the apparent need to neutralize the surface constituents of the ash before $H_2SO_4$ as such can remain. The experimental data show that the concentration of $H_2SO_4$ needed for conditioning increases as the fly-ash basicity increases and, in addition, the total amount of $H_2SO_4$ that must be collected on the ash for adequate conditioning also increases as the basicity increases.

The concluding task was to compare the costs of $H_2SO_4$ conditioning by injection of $SO_3$ or $H_2SO_4$ vapor in the different injection systems operated by the Public Service Company of Colorado. From the cost data supplied by this utility company, the following estimates about capital and operating costs were reached for individual power units with different production capacities and injection rates:

| Injection system | Unit size, MW | Capital cost, dollars | Operating cost, mils/kWh 10 ppm | Operating cost, mils/kWh 20 ppm |
|---|---|---|---|---|
| $SO_3$ evaporation | 125 | 169,000 | 0.0515 | 0.0641 |
| | 250 | 169,000 | 0.0327 | 0.0453 |
| | 500 | 256,000 | 0.0281 | 0.0407 |
| $H_2SO_4$ evaporation | | | | |
| Low temperature | 125 | 288,000 | 0.0770 | 0.0888 |
| | 250 | 375,000 | 0.0542 | 0.0662 |
| | 500 | 570,000 | 0.0440 | 0.0559 |
| High temperature | 125 | 300,000 | 0.0759 | 0.0840 |
| | 250 | 387,000 | 0.0518 | 0.0599 |
| | 500 | 583,000 | 0.0408 | 0.0490 |

In summary, the $SO_3$ evaporation system appears least expensive, primarily as a result of the greater capital cost experienced for the $H_2SO_4$ systems in the installations of the Public Service Company. However, the relative costs of the different systems are subject to change, especially if $H_2SO_4$ injection systems should be installed in greater numbers than they have to date, resulting in reduced capital costs.

# A STUDY OF RESISTIVITY AND CONDITIONING OF FLY ASH

## I. INTRODUCTION

This is the final report of an investigation by Southern Research Institute of the use of chemical conditioning agents to control the electrical resistivity of electrostatically precipitated fly ash in coal-burning electric power stations. This investigation was carried out under Contract CPA 70-149 during the period from July 1, 1970, to August 31, 1971.

### A. Technical Background

For the efficient removal of fly ash from flue gases in an electrostatic precipitator, several conditions must be satisfied. One of the most important conditions is that the electrical resistivity of the ash deposited on collector electrodes shall lie within an appropriate range of values, usually believed to have a lower limit of about $1 \times 10^7$ ohm cm and an upper limit of about $2 \times 10^{10}$ ohm cm.[1,2] Other conditions, however, are of comparable importance and must be satisfied simultaneously. For example, the distribution of gases must be reasonably uniform, the velocity of the gases passing between the corona wires and the collector electrodes must not be excessive, and the power supply must be capable of maintaining an adequate current density at the electrodes.[1,2]

If the resistivity of the collected ash is too low, only a small voltage drop can be maintained across the collected layer. Hence, there will be only a small electrical force holding the ash to the collector electrodes, and the extent of reintrainment of ash particles in the adjacent gas stream may be severe. On the other hand, if the resistivity of the collected ash is too high, either of the following phenomena may occur: (1) The resistance through the collected layer of ash will lower the corona current that can be produced with the normal operating voltage and, as a consequence, the electric field in the gas stream and the resulting migration velocities of negatively-charged fly-ash particles toward the collecting electrodes will be markedly reduced. Usually, an attempt to overcome the effect of excessive resistance through the collected ash with increased voltage and correspondingly increased electric field will meet with failure as the result of the occurrence of rapid sparking (the maximum voltage that can be produced between the corona wires and the collecting electrodes is usually about the same with or without collected dust).[3] (2) The resistance through the collected layer of ash may be sufficient to cause electrical breakdown in the layer with attendant formation of positive gaseous ions ("back corona" or "reverse ionization"), neutralization of negative charges on the ash particles, and reintrainment of the ash particles in the gas stream.

It appears from the literature that problems stemming from low resistivity are rare but those stemming from high resistivity are a fairly common occurrence, especially in power plants burning low-sulfur coals. High resistivity of ash from low-sulfur coal is attributed to the low concentration of $SO_3$ that is produced in the combustion process and the resulting failure of the ash to collect sufficient amounts of $SO_3$ and $H_2O$ vapors from the gas stream to produce a conductive surface film. Owing to the increasing emphasis on the use of low-sulfur coals to minimize emission of sulfur oxides and the simultaneous demands for improvements in fly-ash collection, increasing efforts are being made in the power industry to find satisfactory methods to overcome the problem of high resistivity.

There are, at present, essentially three methods of overcoming the problem of high resistivity of fly ash. One method is to operate electrostatic precipitators at temperatures well below the normal range (e.g., below 250°F), at which enhanced collection of $H_2O$ vapor can produce a sufficiently conductive surface film to make up for the shortage in $SO_3$.[4] Still another method is to operate a so-called "hot precipitator" ahead of the air heater with temperature in excess of 600°F, where the volume conductivity of fly ash (in contrast to the surface conductivity referred to above) is high enough to permit efficient precipitation.[5] Still another method, permitting operating of precipitators at customary temperatures (275 to 325°F) is to inject chemical conditioning agents to make up for the shortage of naturally produced $SO_3$.[6]

Trials of a variety of conditioning agents have been reported in the literature during the past 30 years. The types of agents investigated have included: (1) $H_2O$ vapor (used as a supplement to the $H_2O$ vapor produced during the burning of coal); (2) various acidic agents, typified by $SO_3$ or its analog $H_2SO_4$ (also used as a supplement to the product of coal combustion); (3) various basic compounds, typified by $NH_3$; and (4) various compounds derived from $SO_3$ and $NH_3$, such as $(NH_4)_2SO_4$. Some of the earliest and most extensive work on conditioning was conducted by Chittum.[7] This work was done principally with laboratory equipment rather than with full-scale industrial installations (which would have been more desirable from a practical point of view); even so, the work is still worthy of attention, for it included a wide variety of conditioning agents and a number of different types of particulate substances. Chittum recognized clearly the importance of conditioning agents for increasing the surface conductivities of precipitated solids. He reached the conclusion that, in general, acidic conditioning agents were most effective for treatment of basic solids whereas basic agents were most effective for treatment of acidic solids. In conjunction with this conclusion, he theorized that the adsorption of conditioning agents of opposite acid-base behavior from suspended solids enhanced the adsorption of $H_2O$ vapor and the resulting formation of a conductive surface layer.

Since the work of Chittum was concluded, reports have been published of various trials of conditioning agents in both laboratory facilities and full-scale industrial plants, notably those in the coal-burning power industry. Examples of reported applications of $SO_3$ or the chemically-equivalent substance $H_2SO_4$ have been described by White;[1,8] Busby, Darby, and Whitehead[3,6] (who have discussed the early and highly successful application of $SO_3$ in the Kincardine plant in Scotland); and Watson and Blecher.[9] Examples of reported trials of $NH_3$ and $NH_3$-$SO_3$ salts have been described by Watson and Blecher,[9] Baxter,[10] Reese and Greco,[11] and Dalmon and Tidy.[12] The reports cited here do not include all of the publications relevant to the subject of gas conditioning, but they are representative of the recent literature on the subject. They discuss both highly successful results with conditioning agents, as indicated above for the application of $SO_3$ at Kincardine, and some relatively unsuccessful results, as reported from trials of $SO_3$ in a plant in Australia.[8]

Reference was made above to the chemical equivalence of the chemical substances indicated by the formulas $SO_3$ and $H_2SO_4$. There is experimental evidence that $SO_3$ and $H_2O$ react very rapidly to form $H_2SO_4$ in the vapor state,[13] and that the extent of the reaction is governed by the concentration of excess $H_2O$ and the temperature.[14] Although there are no apparent rate data for the dissociation of $H_2SO_4$ to $SO_3$ and $H_2O$ under conditions where $H_2SO_4$ is unstable, it is reasonable to assume that the dissociation process will also occur rapidly until equilibrium is reached. If a large excess of $H_2O$ is present as in the flue gases produced in coal-burning power plants, the data of Bodenstein and Katayama[14] show that at a representative concentration of $H_2O$, 10% by volume, more than 90% of the total of $SO_3$ and $H_2SO_4$ will occur as $SO_3$ above 700°F and more than 90% will occur as $H_2SO_4$ below 475°F.

## B. Scope of This Investigation

The investigation of conditioning carried out by this Institute under Contract CPA 70-149 was devoted exclusively to the use of conditioning agents in the coal-burning power industry. Furthermore, it was devoted primarily to the use of the agents $SO_3$ and $H_2SO_4$, but it included relatively brief studies of the agents $H_2O$ and $NH_3$. All of the agents except $NH_3$ were used to cope with problems of high resistivity; the agent $NH_3$ was investigated under the relatively rare conditions of low resistivity.

There were two principal reasons for undertaking this research:

- First, several scheduled installations of $SO_3$ and $H_2SO_4$ injection facilities in this country, such as those of the Public Service Company of Colorado, afforded an opportunity to investigate the effectiveness and cost of conditioning by either of these agents under a variety of conditions—(1) coal composition; (2) fly-ash composition, concentration, and particle size; (3) conditioning temperature; and (4) conditioning-agent concentration and injection method. The results of the investigation were expected to provide general guidelines of value to utility companies considering the use of these conditioning agents to cope with high-resistivity problems, permitting prediction of the results to be obtained in new installations and prediction of the costs to be incurred in the plants involved.

- Second, the planned utilization of apparatus designed for _in situ_ determinations of electrical resistivity was expected to show the effectiveness of conditioning in a realistic context. So-called _in situ_ determinations are those made with the appropriate experimental apparatus inserted in the entrance duct of a precipitator both in the absence and the presence of conditioning agent. This approach of making _in situ_ determinations of resistivity is far superior to the approach of removing samples to a laboratory, an approach often used in part despite the known hazard of changes in the surface properties of fly ash following removal from the flue-gas environment. Moreover, consistent use of changes in resistivity as the criterion of effectiveness is much more preferable than the alternative used by some investigators of determining changes in the efficiency of precipitator operation. The basic premise of using $SO_3$ or $H_2SO_4$ as a conditioning agent is that a reduction in surface resistivity is the only direct result to be expected. An improvement in precipitator efficiency will not necessarily follow; certainly it will follow only to a limited degree at best if, for example, the precipitator operates with an excessively high flow rate of flue gases or with electrodes of inadequate surface area or power density. Information obtained by one utility and reported to us on a confidential basis showed that $SO_3$ improved efficiency when the power plant was operated at a power level well below the rated value but with a flue-gas velocity consistent with the precipitator design, whereas $SO_3$ did not improve efficiency during power production at the rated level and gas flow through the precipitator at an excessive rate.

The specific objectives of this investigation may be summarized as follows:

- To determine in general whether fly ash of varying composition derived from coals of varying composition can be effectively conditioned with $SO_3$ or $H_2SO_4$

- To show in specific detail how the effectiveness of conditioning is governed by parameters such as the properties of the fly ash, the concentration of the conditioning agent, and the mode of injection of the conditioning agent

- To formulate theories to explain the mechanisms of conditioning

- To analyze the costs incurred during the use of conditioning agents

## II. EXPERIMENTAL FACILITIES, APPARATUS, AND PROCEDURES

### A. Power-Plant Facilities

The principal tasks of this investigation were carried out on the basis of field studies at various power-generating stations, all burning pulverized coal, and on the basis of supplemental laboratory analyses of samples collected at these plants. As listed in Table 1, five power units with $SO_3$ or $H_2SO_4$ injection systems were investigated, and six other units without $SO_3$ or $H_2SO_4$ injection systems were investigated for comparative purposes. Most of the power stations are identified by names, locations, and owner companies; however, three of the stations are identified only by code letters, in view of requests by the owner companies not to identify these plants explicitly.

Details about the conditions under which each plant was operated are given later in this report as an introduction to the discussion of the experimental studies of that plant. However, Table 1 gives information about some of the most important features of the various plants. Moreover, Figure 1 shows the schematic arrangement of the major elements found in the various plants and referred to in the table——air heater, mechanical collector and electrostatic precipitator for fly-ash removal, and site of injection of $SO_3$ or $H_2SO_4$ conditioning agent. Information in the table shows that mechanical collectors were not present in several of the plants; it also indicates the different sites at which conditioning agent was injected——ahead of the mechanical collector and ahead of the electrostatic precipitator.

### B. Electrical-Resistivity Determinations

During the investigation, use was made of two basic types of apparatus, differing in the mode of sample collection and the design of electrodes. The two types of apparatus are referred to, for convenience, as cyclone and point-plane resistivity probes. They differed primarily as follows: (1) in probes of the cyclone type, centrifugal force is used for sample collection and concentric cylindrical electrodes are used for resistance measurements; (2) in a probe of the point-plane type, electrostatic precipitation is used for sample collection and parallel discs are used as the electrodes for resistance measurements. The design and operation of each type of probe are described briefly in the following paragraphs and more completely in a published article by other investigators[15] and in the final report from the Institute under Contract CPA 70-166.[16]

Table 1. Power-Plant Stations Investigated in the Comparison of Conditioning by Injected and Naturally Produced $SO_3$ or $H_2SO_4$

| Station name | Power unit | Owner company | Location | Facilities for fly-ash removal[a] | Facilities for fly-ash conditioning | |
|---|---|---|---|---|---|---|
| | | | | | Agent | Injection site[a] |
| Cherokee | 2 | Public Service Company of Colorado | Denver, Colo. | MC, EP | $SO_3$ | Before EP |
| X[b] | 4 | — | — | EP | $SO_3$ | Before EP |
| Cherokee | 3 | Public Service Company of Colorado | Denver, Colo. | MC, EP | $H_2SO_4$ | Before MC |
| Arapahoe | 4 | Public Service Company of Colorado | Denver, Colo. | MC, EP | $H_2SO_4$ | Before EP |
| Y[b] | 6 | — | — | EP | $H_2SO_4$ | Before EP |
| Widows Creek | 7 | Tennessee Valley Authority | Stevenson, Ala. | EP | None[c] | — |
| Kingston | 5 | Tennessee Valley Authority | Kingston, Tenn. | MC, EP | None[c] | — |
| Gallatin | 4 | Tennessee Valley Authority | Gallatin, Tenn. | MC, EP | None[c] | — |
| Bull Run | -[d] | Tennessee Valley Authority | Oak Ridge, Tenn. | EP | None[c] | — |
| Z[b] | 1 | — | — | EP | None[c] | — |
| Shawnee | 10 | Tennessee Valley Authority | Paducah, Ky. | MC, EP | None[c] | — |

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a. MC = mechanical collector, EP = electrostatic precipitator.

b. Identified only by code letter at the request of the owner company.

c. "None" signifies no facility for injection of either $SO_3$ or $H_2SO_4$. The Widows Creek unit, however, has permanent facilities for $NH_3$ injection, and the Kingston unit had temporary facilities for $H_2O$ injection during one series of field tests.

d. The Bull Run Station consists of only one very large power unit.

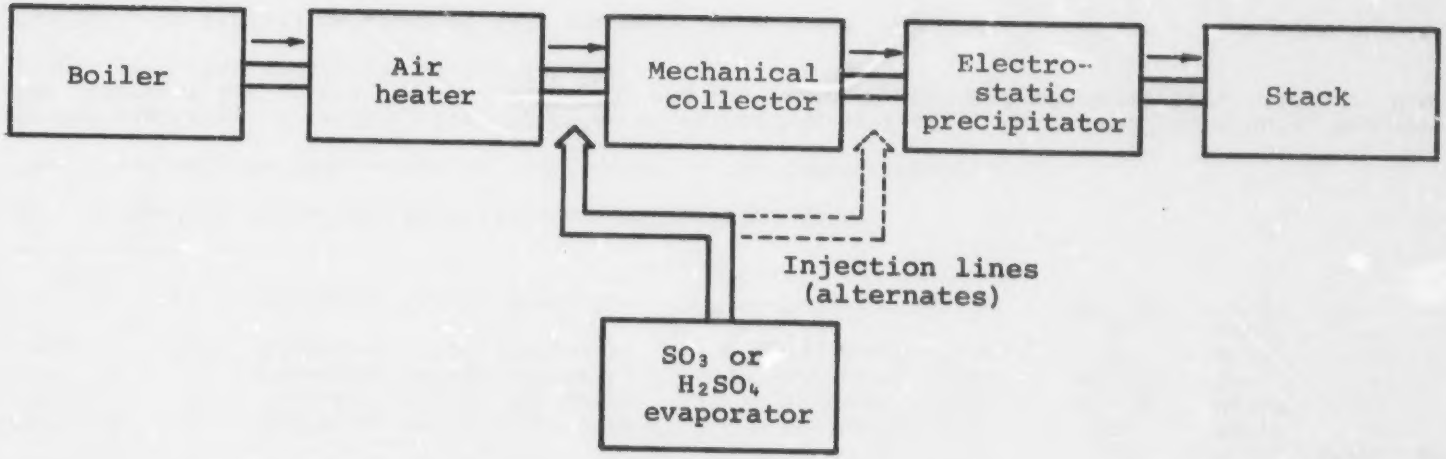
Boiler
Air heater
Mechanical collector
Electro-static precipitator
Stack
Injection lines (alternates)
SO$_3$ or H$_2$SO$_4$ evaporator

Figure 1. Schematic Diagram Showing the Major Components of the Various Power Plants Investigated during this Program

## 1. Cyclone probes

### a. Design developed by Cohen and Dickinson

A cyclone probe developed and described by Cohen and Dickinson[15] was made available for use during this investigation through the courtesy of Lodge-Cottrell Limited. From a literal point of view, this device is a "probe" only in the sense that it includes a pipe for insertion into the duct from which a fly-ash sample is to be taken. Other important components of the device——the cyclone in which the sample is collected by centrifugation from a high-velocity gas stream, and the cylindrical resistivity cell to which the sample is transferred by a rapping procedure——are located in an insulated chamber placed outside the flue but maintained at the duct temperature with two internal space heaters.

During this investigation, it was found that several modifications were desirable to ensure satisfactory use of the Cohen-Dickinson probe. One modification consisted of wrapping heating tape and insulation around the sampling pipe to avoid a decrease in temperature of the sample between the duct and the cyclone. Other modifications consisted of placing thermocouples in the sampling line and on the wall of the resistivity cell to ensure that temperatures in these locations were controlled at the temperature in the duct.

Resistances of collected samples were determined by applying a voltage of 1.0 kV across the electrodes and measuring the flow of current thus produced. The electrodes had a common height of 3.8 cm and diameters of 0.4 and 1.4 cm about a common axis. The average value of the electric field produced in the annular sample between the electrodes was 2.0 kV/cm. Typically, with constant voltage applied, the current gradually decreased with time and appeared to approach a final value about one order of magnitude lower than the initial value, as illustrated by typical data in Figure 2.* The decrease in current was attributed to slow changes in the surface chemistry of the sample, and the initial current reading was therefore taken as the best value for calculating resistance. Sample resistivities were computed from the initial resistances, the diameters of the electrodes, and the height of the electrodes.

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* This and other phenomena that complicate the task of obtaining reliable *in situ* resistivity values are discussed later in this report and in another report from this laboratory.[16]

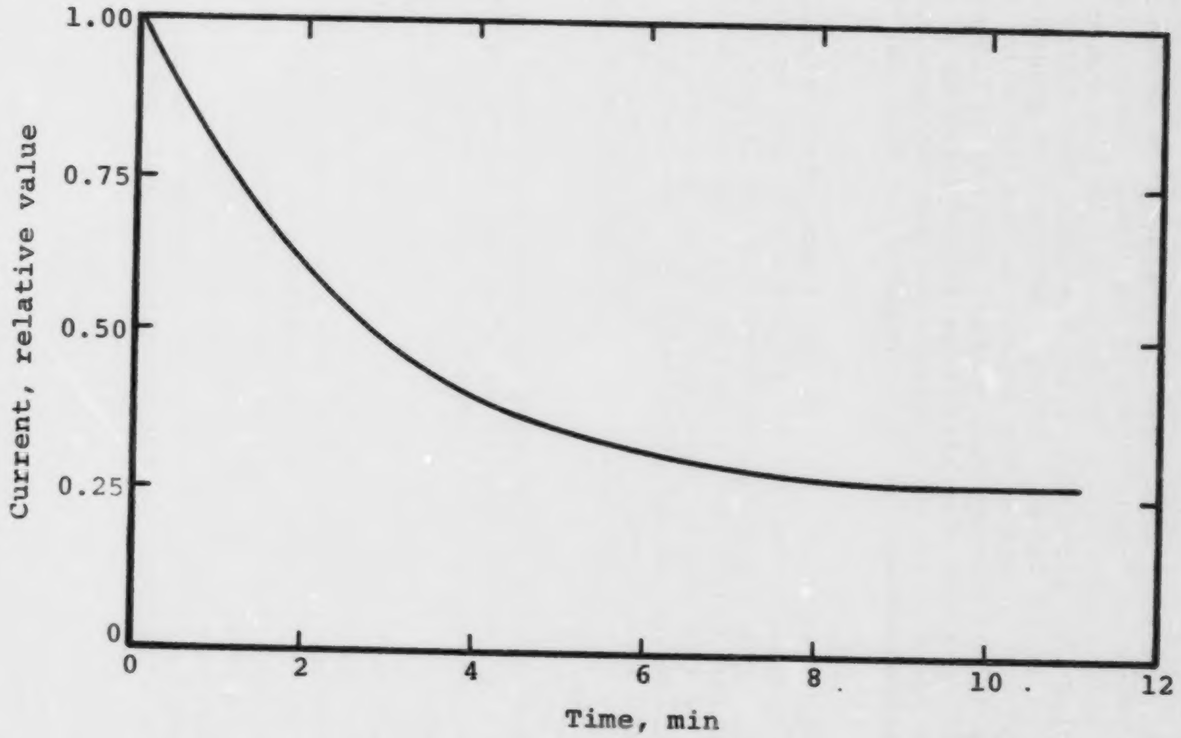

Figure 2. Observed Variation in Current with Time with Fly Ash Collected in a Cyclone Sampling Apparatus

With the procedure outlined above, the Cohen-Dickinson probe was used with fair success on several occasions. Ultimately, however, it was replaced with an Institute-designed probe that offered as its principal advantage a shortening of the time required for temperature equilibration prior to sampling.

### b. Design originated in this laboratory

The essential components of a second cyclone probe that was designed and fabricated in this laboratory were a cyclone sample collector and a cylindrical resistivity cell with dimensions similar to those in the Cohen-Dickinson apparatus. The height of the electrodes was 4.4 cm and the diameters were 0.47 and 1.27 cm. In contrast to the cyclone and cell in the Cohen-Dickinson device, these components of the Institute apparatus were mounted at the end of a pipe that was inserted directly approximately 1 m into the duct where samples were collected. The samples were pumped into the cyclone through a rectangular slot and the effluent gases were then discharged through the pipe, which served as a connection to a high-volume pump as well as a mount for the cyclone and the cell. A thermocouple was placed at the extremity of the assembly (the base of the cell) to indicate the time when temperature equilibration in the duct had been reached and sampling could be started.

Electrical measurements and calculations were made with the modified cyclone probe by the same procedures as with the Cohen-Dickinson probe. With the usual applied voltage of 1.0 kV the average electric field in the sample during resistivity measurements was 2.5 kV/cm, only slightly higher than that in the Cohen-Dickinson apparatus. The current through the samples in both cyclone probes showed a similar time dependence; thus, the initial current was used for calculating resistivity in the Institute probe as in the Cohen-Dickinson probe.

## 2. Point-plane probe

The essential components of a point-plane probe constructed in this laboratory were a tapered rod of stainless steel to serve as a source of negative corona, a copper disc with an area of 5 $cm^2$ located centrally about 3.8 cm from the corona source, and a second disc with about the same area but with a small opening in the center to permit movement along the axis of the corona source. The electrodes (the corona source and the two disc electrodes) were mounted on the end of an aluminum pipe, which permitted insertion of the electrodes into the duct for a distance of about 1 m. A perforated shield was placed around the electrodes to avoid excessive gas turbulence near the electrodes but, at the same time, to permit gas migration into the electrode area. A thermocouple was placed near the electrodes to indicate the time when temperature equilibration in the duct occurred.

The procedure of collecting a sample consisted of applying a voltage of about 15 kV between the corona source and the first disc electrode described above, with the second disc electrode retracted from the corona region. After sample collection was completed, the power supply providing the current was disconnected, and the second disc electrode was moved into contact with the deposited ash on the first electrode. A spring was used to produce a compressive force on the deposited ash, and the thickness of the deposit——usually, about 0.1 cm——was then determined by means of a gage that indicated the separation between the two disc electrodes. Except in unusual circumstances, such as those encountered in one power station that is discussed in Section III.A.1, the resistance of the sample was determined by applying various voltages across the deposit and measuring the corresponding currents at electric fields in the range from about 1 to 20 kV/cm (the upper limit with each sample was the field required for electrical breakdown to occur). The resistivity of the sample was then calculated by multiplying the resistance of the sample by the factor A/h, where A was the electrode area (5 $cm^2$) and h was the sample thickness.

Negligible time-dependence of resistivity data obtained with the point-plane apparatus was observed in contrast with the marked time-dependence observed with the two cyclone probes. However, marked electric-field dependence of the data recorded with the point-plane apparatus was usually encountered. Figure 3 summarizes data that were obtained in one of the field studies (at the Kingston Station, which is discussed in Section VI.A). The curve plotted in this figure shows the relative values of resistivity in the range of electric fields up to 12 kV/cm. The data points at 2, 4, 8, and 12 kV/cm compare the calculated average ratios of resistivities observed at these fields to the resistivity observed at 1 kV/cm; the bars show the maximum range in individual experiments. Extrapolation of the curve was made to the vertical axis to show the approximate relative value of resistivity at fields lower than the minimum of 1 kV/cm that was employed experimentally. Presumably, a field dependence of resistivity data obtained with the cyclone probes would have been observed if it had been possible to discern the effects from field variation in the presence of marked changes in resistivity with the time of measurement.

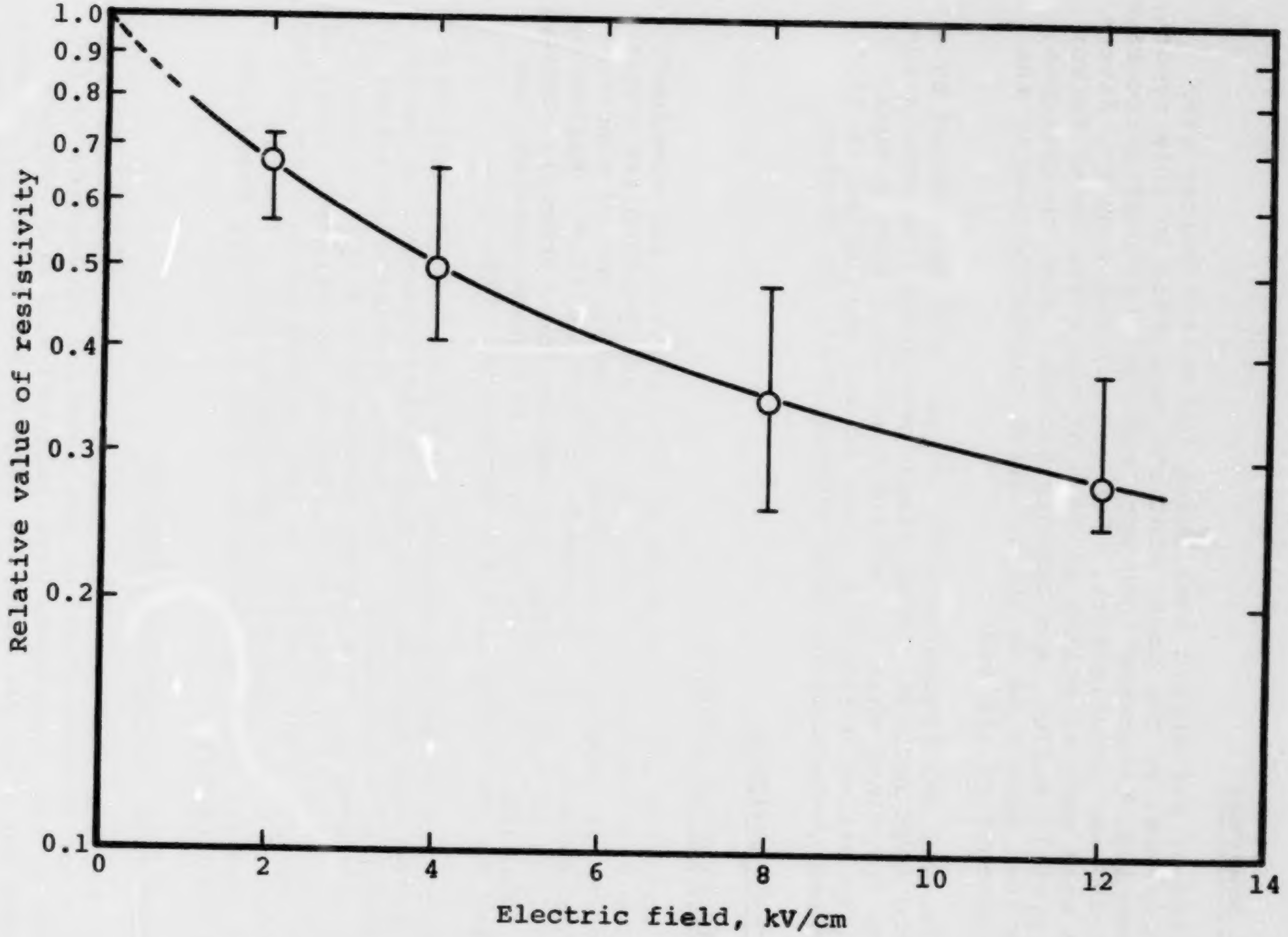

Figure 3. Observed Variation of the Resistivity of Fly Ash with Electric Field in One Power Plant (Kingston Unit 5)

## C. Coal Analyses

Samples of pulverized coal being fed to the boiler were collected in most of the power stations discussed in this report. For all samples, determinations were made of the total percentages of sulfur and ash constituents. For some of the samples, determinations were made of sulfur in each of the three major forms: sulfate, pyritic sulfur, and organic sulfur. Also on occasion, determinations were made of the relative concentrations of the major components of the ash.

Sulfur and ash concentrations in coal were determined by established ASTM methods. Each sample was ground to pass a 60-mesh sieve (provided that it had not previously been ground sufficiently before collection), and it was then dried at 110°C and processed chemically by ASTM Methods D-271 and D-2492.

## D. Fly-Ash Analyses

### 1. Collection of samples

The majority of the samples of fly ash used for chemical analyses were collected with the cyclone and point-plane resistivity probes at sampling ports near the entrances of electrostatic precipitators, as discussed in Section II.B. Following determinations of resistivity, the samples were promptly removed from the sampling probes, stored in polyethylene bottles, and transported to the laboratory for analytical work.

Most of the remaining samples used for chemical analyses were collected with cyclone sampling probes inserted in ports located ahead of air heaters. The Cohen-Dickinson resistivity apparatus was used in this manner simply as a sample collector in some of the initial field work, but it was replaced later with an all-metal apparatus similar to the cyclone probe constructed at the Institute for resistivity determinations. The few remaining samples were collected by methods briefly described later in this report.

### 2. Analyses by wet-chemical methods

This section discusses the procedures that were used most frequently for determination of the chemical properties of fly ash. Some of the procedures were followed with all samples; others were not followed with all samples but nevertheless were used with sufficient frequency to represent a substantial part of the overall analytical effort. On occasions cited later in this report, variations in these procedures were made in special circumstances, and still other procedures were followed to obtain supplemental information.

### a. Determination of pH produced in an aqueous slurry

One of the procedures routinely used in the analyses of fly-ash samples was to prepare a slurry of ash with distilled water and determine the equilibrium value of the pH reached after prolonged stirring. Each sample of ash was mixed with water in the ratio of 0.1 g of ash to 30 ml of water. Usually, the equilibrium pH was reached in about 30 min, but sometimes the slurry was stirred for 60 min to ensure that equilibrium had been established. During the time required for equilibration, each slurry was protected from ambient air to avoid absorption of atmospheric $CO_2$. Approximately the same value of pH was recorded during the final period of stirring or after stirring had been stopped and the suspended ash particles had been removed from the liquid phase by settling or centrifugation.

The procedure used for determining pH was similar to a procedure reported in the past by Lee, Friedrich, and Mitchell.[17] From the standpoint of convenience, it was preferred to an alternative procedure described by White,[8] which involved extraction with hot water in Soxhlet apparatus.

### b. Determination of the excess of base or acid soluble in water.

During the initial phase of this investigation, the fly-ash samples consistently showed that they contained an excess of soluble base—that is, they produced pH values in aqueous slurries that were substantially above the neutral value of pH 7. For several of these samples, the liquid phase from the slurry was separated from the residual ash by centrifugation; then the liquid was titrated to pH 7 with a solution of HCl, with a pH meter for recording pH *versus* added HCl. From the results of the titration, the quantity of water-soluble base in the original ash was calculated as the equivalent weight percentage of CaO in the ash, assuming that only CaO had dissolved as $Ca^{+2}$ and $OH^-$ ions.

Several of the samples contained basic substances other than compounds dissolving to produce $OH^-$ ion. This conclusion was based on a comparison of the titration curves obtained with the pH meter in experiments with extracts of fly ash and with solutions containing $OH^-$ ion as the only base present. The soluble basic substances ion may have included silicate and aluminate ions; the titration curves of several fly-ash extracts resembled the curves obtained with synthetic mixtures containing silicate and aluminate ions. Clear-cut identification of bases other than $OH^-$ ion by the titration procedure was not attempted, however, because the locations of inflections in the titration curves of fly-ash extracts were usually not distinct and could have been caused by a variety of other bases than those suggested as possible components.

In later work, several fly-ash samples were found to contain excess acid rather than excess base, in view of the fact that they produced pH values in aqueous slurries considerably lower than pH 7. Extracts of these samples were titrated to pH 7 with NaOH, and attempts were made to interpret the titration curves thus obtained. It was clearly shown that the acids neutralized below pH 7 were largely substances other than $H^+$, probably including hydrated $Al^{+3}$ and $Fe^{+3}$ ions.

### c. Determination of total soluble sulfate

Knowledge of the quantity of sulfate present in fly ash was of particular interest, in view of the fact that this property was indicative of the amount of $SO_3$ or $H_2SO_4$ deposited on the ash during conditioning in the presence of flue gases. Determination of sulfate in forms soluble in water was, therefore, a procedure routinely used in fly-ash analyses, as in previous work described by White.[8]

Water-soluble sulfate was assumed to be present primarily on the fly-ash surface, as concluded by White[1,8] and confirmed in other work discussed subsequently in this report. This component of the ash was determined by the following steps: (1) treatment of an aqueous extract prepared during the pH determination with a sulfonate ion-exchange resin to replace interfering cations with $H^+$ ion, as described by Fritz and Yamamura;[18] (2) dilution of the aqueous $H_2SO_4$ solution resulting from the ion-exchange process with excess isopropanol, producing a water:isopropanol ratio of 1:4; and (3) titration of the resulting solution of $H_2SO_4$ in the mixed solvent with $Ba(ClO_4)_2$ as the titrant and thorin as the indicator, as described by Fritz and Yamamura[18] and by Fielder and Morgan.[19]

### d. Determination of soluble $SO_4^{-2}$ as $H_2SO_4$

In determining the pH of slurries of fly ash from several sources, an interesting dependence of pH on the time of stirring was noted. Immediately following addition of fly ash to distilled water with a usual pH of about 5.5 (showing the presence of absorbed atmospheric $CO_2$), a rapid decrease in pH was observed. Then, with increased time of contact between the ash and the water, an increase in pH occurred until finally an equilibrium value was reached——sometimes below 7 and sometimes substantially above 7.

A minimum in pH with increasing time of contact was assumed to indicate that free acid—probably $H_2SO_4$ on conditioned ash—occurred in the outermost surface layer and thus dissolved first, but that basic substances occurred in the underlying surface layers and ultimately partly or completely neutralized the acid dissolved initially.

Near the conclusion of the contract, efforts were made to find a means of confirming the above hypothesis. Several pure alcohols and alcohol-water mixtures were used for extracting fly-ash samples, and a pH meter was used to indicate whether free acid could be extracted selectively, even in the presence of excess base. The results of these experiments appeared to be quite promising, as indicated in the following paragraph.

In an ethanol-water mixture consisting of 95% of ethanol and 5% of water by volume, several fly-ash samples produced steadily decreasing values of pH until an equilibrium value well below that of the solvent was reached, whereas in water the same fly-ash samples produced an initial decrease in pH and then a sharp rise in pH to values far above pH 7, even up to pH 10 or 11. On the other hand, in the mixed solvent, still other fly-ash samples caused essentially no change or a slight increase in pH. It was concluded, therefore, that some samples contained free acid, whereas others did not. Finally, it was discovered that if an acidic extract was separated from the residual ash and titrated with a solution of NaOH in the ethanol-water mixture, the titration curve observed with the pH meter was practically identical to the titration curve obtained with a synthetic mixture of $H_2SO_4$, ethanol, and water. (To facilitate rapid equilibration of the pH meter in work with the mixed solvents, it was found expedient to add KCl to the mixture at a concentration of $1 \times 10^{-3}$M.)

On the basis of the observations described above, the following procedure was adopted as a means of determining the amount of free $H_2SO_4$ on fly ash: A sample of 0.1 g of fly ash was stirred with 15 ml of the mixed solvent for 10 to 15 min until the pH reached a stable value. If the pH was lower than that of the original solvent, the liquid phase was then separated from the residual ash by centrifugation and titrated with an ethanol-water solution of NaOH with the pH meter as an indicator of the endpoint. The apparent concentration of $H_2SO_4$ as a weight percentage of the ash was then calculated.

In an effort to confirm that $H_2SO_4$ was, indeed, selectively extracted, attempts were made to show that the amount of $SO_4^{-2}$ ion extracted was equivalent to the amount of acid extracted.

Generally speaking, these attempts were not successful. Although $SO_4^{-2}$ was found, it was not found in amounts precisely equivalent to the acid. However, the method used for determining $SO_4^{-2}$—based on titration with $Ba(ClO_4)_2$ with thorin as indicator—lacked the sensitivity and precision needed to obtain accurate determinations of $SO_4^{-2}$ at concentrations equivalent to the concentrations of acid found.

Despite the generally poor agreement between concentrations of acid and $SO_4^{-2}$ found in the ethanol-water extracts, it is felt that the results of the acid determinations show with fair certainty that free $H_2SO_4$ did, indeed, exist on a number of the fly-ash samples—even on several samples that had been stored in the laboratory for several months before they were analyzed.

### 3. Analyses by optical methods

Studies of the chemical compositions of a few fly-ash samples were made by the methods of X-ray diffraction and electron-microprobe analysis. It was assumed that the method of X-ray diffraction might be of value for identifying specific compounds in the ash, provided they exist in crystalline form, and that the method of electron-microprobe analysis might be useful for determining specific elements on the surfaces of ash particles.

X-Ray diffraction. Analysis of fly-ash particles by the method of X-ray diffraction indicated that the ash consisted largely of amorphous rather than crystalline substances. Analysis of soluble components of the ash—isolated by dissolution in water and subsequent drying—failed to give an identifiable diffraction pattern. Thus, X-ray diffraction appeared to be of limited value as an analytical method in this investigation.

Electron-microprobe analysis. In view of the paramount interest in the presence of sulfur as $SO_4^{-2}$ ion on the surfaces of fly-ash particles, electron-microprobe analysis was investigated as an alternative method for determining sulfur. The method, not heretofore employed in studies of fly-ash conditioning, proved to be of value for studies of the distribution of sulfur on various particles and for semiquantitative determinations of sulfur concentrations.

One matter of interest was to determine the relative distributions of sulfur on the original surfaces of fly-ash particles and on cross sections of particles that had been exposed by polishing. Sulfur was readily detected on the original surfaces but was not found in the interior material.

Another question investigated was how the sulfur was distributed among a large group of particles. Nearly all of the particles analyzed contained detectable amounts of sulfur; however, a small number of particles contained unusually large amounts of the element. No correlation was found between sulfur concentration and parameters such as particle color, magnetism, and other elemental components——predominantly iron and silicon in some instances and calcium, silicon, and aluminum in others. However, all of the particles containing exceptionally high concentrations of sulfur were, for some unexplained reason, agglomerated with other smaller particles.

In one of the samples analyzed quantitatively, it was found that approximately 99% of the particles contained about 0.1% of sulfur, and the remaining 1% contained up to 5% of sulfur. Analysis of this sample by the wet-chemical method previously described showed that the sample contained 0.72% of water-soluble $SO_4^{-2}$, the equivalent of about 0.24% of sulfur. The agreement between the two results seems reasonably satisfactory.

In two more samples, quantitative analyses were made of aggregates of particles with an enlarged electron beam——approximately 10 µm in diameter, compared with the number-median particle diameter of about 1.5 µm. One of the samples had been collected in the absence of $SO_3$ conditioning agent; the microprobe analysis showed that it contained 0.4% of sulfur, compared with the calculated value of 0.5% of sulfur based on the experimental finding of 1.5% of soluble $SO_4^{-2}$. The second sample had been collected with $SO_3$ conditioning agent added; the microprobe analysis showed that it contained 0.7% of sulfur, compared with the calculated value of 1.0% based on the experimental finding of 3.0% of soluble $SO_4^{-2}$. As in the analyses of individual particles, the results of microprobe analyses of aggregates of particles seem to agree satisfactorily with the results obtained by the wet-chemical procedure.

For routine use, determination of sulfur as $SO_4^{-2}$ ion by the wet-chemical procedure appeared to be preferable to determination by electron-microprobe analysis. However, the validity of the chemical method for showing the amounts of $SO_4^{-2}$ collected on the surfaces of the particles after injections of $SO_3$ conditioning agent was strengthened by the results of the electron-microprobe analyses, especially the findings that sulfur was located primarily on the particle surfaces and distributed with sufficient uniformity on all particles to have a significant effect on electrical resistivity.

### 4. Determinations of particle-size distribution

Particle-size distributions in fly-ash samples were determined by a microscopic technique with visible radiation. Approximately 25 mg of each sample was suspended in 2 ml of glycerine; approximately 50 µl of the suspension was then spread on a microscope slide and protected with a cover. Particles in different size ranges (<2, 2-5, 5-10, 10-25 and >25 µm) were counted by use of a microscope equipped with a MSA Dust View Microprojector (product of Mine Safety Appliances Company). The microscope and projector allowed viewing of the fly-ash particles at a magnification of 1000 diameters on a 200- by 250-mm screen with a calibrated grid. Usually, a total of 300 to 400 particles was counted in six to ten fields on the slide, each approximately 0.20 mm high and 0.25 mm long.

In each sample, most of the particles smaller than 10 µm were translucent spheres. Most of the particles larger than 10 µm were also spherical but a substantial fraction were opaque rather than translucent. There were relatively few agglomerates of spherical particles and other particles of irregular shape. The agglomerates and irregular particles in various size ranges were counted on the basis of their maximum dimensions.

Percentages of each sample in the various size ranges were calculated on the number basis and plotted on logarithmic probability paper. As a rule, the plotted data fell near a straight line, signifying a log-normal particle-size distribution. The intersection of the coordinate for 50% probability with the straight line representing the data points was recorded as the number-median particle diameter.

## E. Flue-Gas Analyses

### 1. Collection of $SO_3$ and $SO_2$ samples

The components of flue gases that were of paramount importance during this investigation of gas conditioning were $SO_3$ and $H_2SO_4$. As indicated previously in this report, the relative concentrations of $SO_3$ and $H_2SO_4$ vapors in flue gases depend upon both the temperature and the concentration of $H_2O$ vapor, assuming that chemical equilibrium involving $SO_3$, $H_2SO_4$, and $H_2O$ vapors is continously maintained. However, $SO_3$ and $H_2SO_4$ are not distinguishable by the analytical methods employed during this investigation; thus, for convenience in discussions of flue-gas analyses, the formula $SO_3$ is used to indicate both chemical substances.

Another component of flue gases that was of considerable interest was $SO_2$. This compound is ineffective as a conditioning agent. However, $SO_2$ is a potential source of $SO_3$ through reaction with $O_2$, and it is a practical indicator of the percentage of sulfur in the fuel. Thus, the concentration of $SO_2$ was routinely determined along with the concentration of $SO_3$.

### a. Survey of available collection methods

Collection of the $SO_3$ in flue gases is a difficult problem because (1) $SO_3$ is easily lost as the result of condensation with excess $H_2O$ to form liquid $H_2SO_4$-$H_2O$ mixtures if high temperatures are not maintained in the sampling line between the source and the collector and (2) $SO_3$ normally occurs in flue gases at low concentrations in the presence of a large excess of a probable interferant, $SO_2$, which can be oxidized to $SO_3$ by $O_2$. Examples of methods that have been used by various investigators in efforts to overcome these sources of difficulty are described briefly below. All of the methods use a heated sampling probe fitted with a filter to remove the fly-ash particles and any liquid particles of a condensed $H_2SO_4$-$H_2O$ mixture that may be present; however, they use different types of apparatus to collect samples as a $SO_4^{-2}$ salt or as $H_2SO_4$, as follows:

- The flue gases are pumped through a bubbler filled with a solution of NaOH and an oxidation inhibitor, such as benzyl alcohol. The $SO_3$ and $SO_2$ are collected in the solution as $SO_4^{-2}$ and $SO_3^{-2}$ salts, respectively. The conversion of $SO_3^{-2}$ to $SO_4^{-2}$ is repressed by the presence of the oxidation inhibitor, and each ion may be determined in the presence of the other.[20,21]

- The flue gases are pumped through a bubbler filled with a 4:1 mixture of isopropanol and water, which collects $SO_3$ with much higher efficiency than $SO_2$. Any $SO_2$ collected with the $SO_3$ is removed with a purge of inert gas, such as $N_2$, to avoid interference in the analysis of the sample.[22,23]

- The flue gases are pumped through a condenser coil maintained below the dew points of $SO_3$-$H_2O$ mixtures but above the dew points of other vapor mixtures or individual vapors, such as an $SO_2$-$H_2O$ mixture or $H_2O$ vapor alone. A satisfactory range of condenser temperatures is 140 to 195°F.[24,25]

In contrast to the collection of $SO_3$, the collection of $SO_2$ is a reasonably simple task. In a sampling train that contains either a condenser or an isopropanol-water mixture as the collector for $SO_3$, a bubbler filled with a 3% solution of $H_2O_2$ in water may be used downstream from the $SO_3$ collector to collect $SO_2$ as $H_2SO_4$.

Both condensation and absorption methods for collecting $SO_3$ were thoroughly evaluated under laboratory conditions before they were used in field studies, as described in the following paragraphs. The absorption method for collection $SO_2$, on the other hand, appeared clearly suitable for field use and was not subjected to preliminary evaluation under laboratory conditions.

### b. Evaluation of the condensation method for collecting $SO_3$

The apparatus used for collecting $SO_3$ by the condensation method is similar in design to that described by Lisle and Sensenbaugh.[24] It is shown schematically in Figure 4 as part of a sampling train that includes an absorber for $SO_2$.

The sampling probe includes two concentric tubes with lengths of 1.2 m; the inner tube or sampling line is made of Pyrex with an internal diameter of about 7 mm, and the outer tube used for support and insulation is made of stainless steel with an external diameter of about 25 mm. The annulus between the two tubes contains an electrical heating tape around the wall of the Pyrex tube and an insulating asbestos tape around the heating tape. The end of the Pyrex tube that is inserted in the flue is packed with quartz wool to prevent particles of fly ash and $H_2SO_4$-$H_2O$ condensate from entering the collection system; the other end of the Pyrex tube is fitted with a ball-and-socket joint for connection to the condenser. The condenser consists of a helical condensation tube made from Pyrex tubing with an internal diameter of about 7 mm and an overall length of about 1 m; a spray trap consisting of a fritted-glass filter (sealed to the helix near the exit); a heated bath of ethylene glycol and water around the helix and filter; and a steel pipe fitted with an external heating tape for containing and heating the water-glycol mixture. The $SO_2$ scrubber is a bubbler filled with a 3% solution of $H_2O_2$ in water. The flow-rate indicator is a Charcoal Test Meter (product of American Meter Company) with an inlet filter of Drierite or, as an alternative, a vapor trap immersed in ice water. The Charcoal Test Meter registers the integral of flow rate and time and, thus, shows the total volume of dry flue gases sampled except for the relatively small volumes of $SO_3$ and $SO_2$ collected upstream. A small vacuum pump (Model 1031-V102-351 of Gast Manufacturing Corporation) is used for sampling flue gases at an approximate rate of 2 l/min for a period of about 20 min.

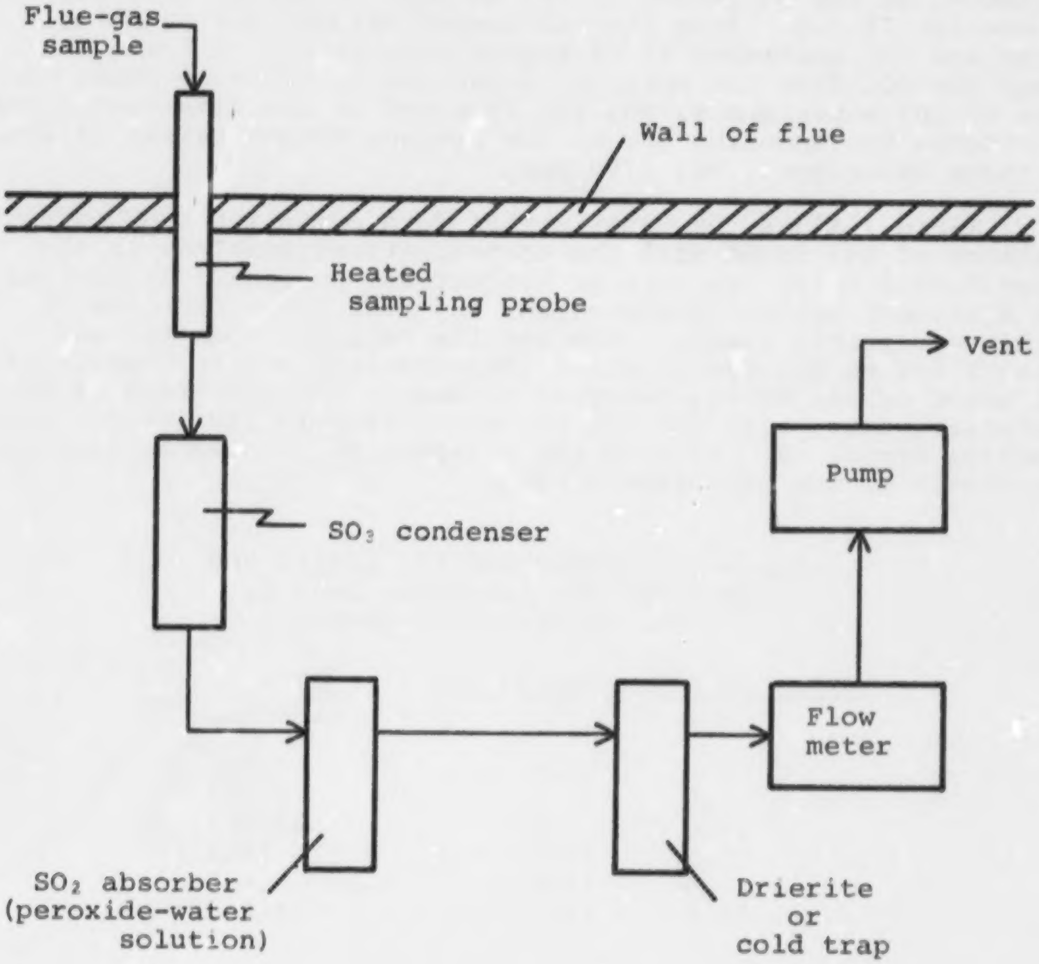
Flue-gas sample
Wall of flue
Heated sampling probe
Vent
Pump
SO₃ condenser
Flow meter
SO₂ absorber (peroxide-water solution)
Drierite or cold trap

Figure 4. Schematic Diagram of Apparatus for Collection of $SO_3$ by the Condensation Method

The performance of the above apparatus was evaluated in the laboratory by injecting aqueous $H_2SO_4$ at known rates in the sampling probe (heated to a sufficient temperature to volatilize both the $SO_3$ and the $H_2O$ added) and determining the amounts of $SO_3$ collected in the condenser by the methods described subsequently in Section II.E.2. Room air was pumped through the sampling probe and the condenser at an approximate rate of 2 l/min to sweep the $SO_3$ from the point of injection to the condenser. In some of the experiments, $SO_2$ was injected in the airstream before it entered the sampling probe; the average concentration of $SO_2$ in these experiments was 1700 ppm.

Table 2 lists the experimental data comparing the concentrations of $SO_3$ found with the concentrations sampled, in the range from 0 to 20 ppm with or without $SO_2$ present. In general, the agreement between observed and injected concentrations is within acceptable limits. The results obtained when $SO_2$ was present but no $SO_3$ was injected indicate that slight degrees of oxidation of $SO_2$ to $SO_3$ occurred either in the airstream or the condenser; thus, with low $SO_3$ concentrations in flue gases, small positive errors may occur in the observed $SO_3$ concentrations as the result of the oxidation of $SO_2$.

Table 2. Comparison of Sampled and Observed $SO_3$ Concentrations by the Condensation Method

| Concn of gas sampled, ppm | | Concn of $SO_3$ found, ppm[a] |
|---|---|---|
| $SO_3$ | $SO_2$ | |
| 0 | 1700 | 0.8-0.9 |
| 2.0 | 0 | 1.7-2.0 |
| 15.6 | 0 | 13.3-15.9 |
| 15.6 | 1700 | 15.9 |
| 17.0 | 1700 | 18.3 |
| 19.8 | 1700 | 15.2-18.1 |

---

a. Based on sample analyses by the methods described in Section II.E.2. Results from multiple determinations are shown as a range of values.

### c. Experimental study of the isopropanol-water absorption method for collecting $SO_3$

Components of the apparatus used for collecting $SO_3$ by absorption in a 4:1 mixture of isopropanol and water are shown schematically in Figure 5. Except for the $SO_3$ absorber, the components of this apparatus are the same as those described above in connection with the condensation method. The absorber for $SO_3$ and the auxiliary absorber for $SO_2$ are made of Pyrex as described in a publication of Shell Development Company.[23] They consist, in essence, of a bubbler filled with the isopropanol-water mixture for collecting $SO_3$ and a second bubbler filled with a peroxide-water mixture for collecting $SO_2$. Both bubblers were immersed in ice-water mixtures to optimize collection efficiencies. Following a period of flue-gas sampling, a stream of nitrogen is passed through the two bubblers to transfer any $SO_2$ in the isopropanol-water mixture to the peroxide-water mixture.

The effectiveness of the apparatus for collecting $SO_3$ was evaluated in the laboratory by the procedures previously described in the discussion of the condensation method. The experimental data are listed in Table 3. These data, like those obtained with the condensation method, indicate that the efficiency of $SO_3$ collection was, in general, satisfactory. The results obtained with $SO_2$ present but with $SO_3$ absent, however, indicate that significant positive errors in $SO_3$ concentrations are to be expected in the range of low values, as the result of the oxidation of $SO_2$ to $SO_3$.

Table 3. Comparison of Sampled and Observed $SO_3$ Concentrations by the Absorption Method

| Concn of gas sampled, ppm | | Concn of $SO_3$ found, ppm[a] |
|---|---|---|
| $SO_3$ | $SO_2$ | |
| 0 | 1200 | 3.1 |
| 2.0 | 0 | 1.8-2.0 |
| 17.0 | 1200 | 16.5-18.4 |
| 25.0 | 0 | 24.6 |

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[a] Based on sample analyses by the methods described in Section II.E.2. Results from multiple determinations are shown as a range of values.

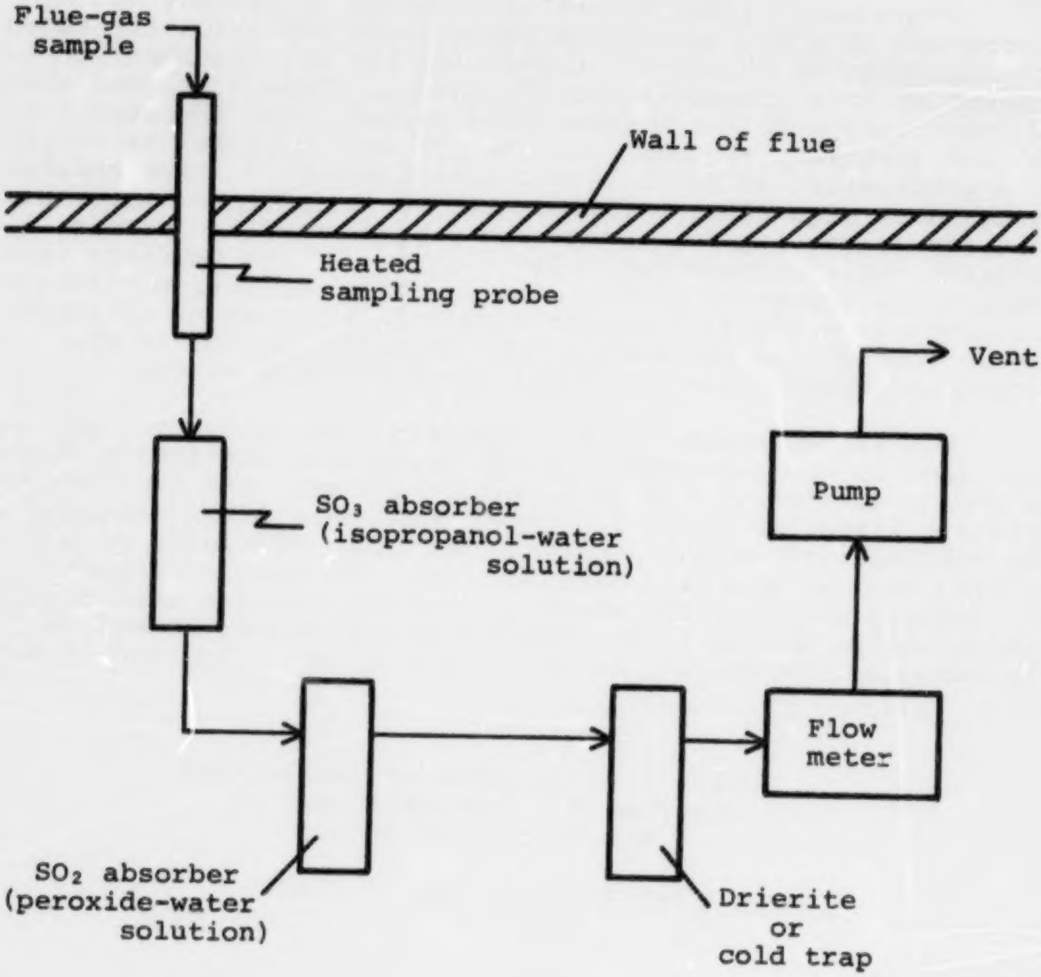
Flue-gas sample
Wall of flue
Heated sampling probe
Vent
Pump
SO₃ absorber (isopropanol-water solution)
Flow meter
SO₂ absorber (peroxide-water solution)
Drierite or cold trap

Figure 5. Schematic Diagram of Apparatus for Collection of $SO_3$ by the Method of Absorption in an Isopropanol-Water Solution

### d. Field studies

During the initial field studies, use was made of both of the collection methods discussed above for collecting $SO_3$ and $SO_2$ samples. Good agreement was obtained by the two methods and thus, in time, either of the methods was considered satisfactory. However, on the basis of convenience, the condensation method was considered preferable and was adopted for routine use.

## 2. Analyses of $SO_3$ and $SO_2$ samples

Two methods were investigated under laboratory conditions for determining the $SO_3$ and $SO_2$ collected as $H_2SO_4$ by either of the two collection procedures. One method was based on titration of $H_2SO_4$ with $Ba(ClO_4)_2$, with a 4:1 mixture of isopropanol and water as the solvent and the organic dye thorin as the indicator of the endpoint.[18,19] The second method was based on treatment of the collected $H_2SO_4$ with excess solid barium chloroanilate and spectrophotometric determination of the chloroanilate ion released in the solution during formation of $BaSO_4$ in place of the original barium chloroanilate.[26] The intensity of ultraviolet absorption at 310 nm was used for calculating the original concentration of $H_2SO_4$.

Our experience showed that the titration method was substantially less sensitive, requiring roughly 25 times as much sample as the spectrophotometric method. The titration method was, on the other hand, far more convenient in terms of the time and the apparatus required for a determination. Moreover, it was sufficiently sensitive for use in determining $SO_3$ in flue gases at concentrations down to 1 ppm with samples of reasonable volumes (e.g., 40 liters), and it was sufficiently sensitive in determining the characteristically much higher concentrations of $SO_2$. In numerous sample analyses by the two methods, the results obtained by the two methods were in good agreement. Thus, we considered the titration method preferable, especially in field work where simplicity was of considerable importance.

## 3. Determination of $H_2O$ vapor

In addition to $SO_3$ and $SO_2$, $H_2O$ was one of the components of flue gases that was of vital importance in the investigation of gas conditioning. In contrast to $SO_3$ and $SO_2$, however, $H_2O$ did not vary widely in concentration. Thus, concentrations of $H_2O$ were determined consistently in every plant but on a less frequent basis than those of $SO_3$ and $SO_2$.

The technical literature is not clear about the methods that may be used most successfully for determining the concentration of $H_2O$ vapor in flue gases. The detailed analytical information of Cuffe et al[27,28] about flue-gas compositions, for example, includes data on $H_2O$ concentrations but gives no description of the method used to obtain there data. On occasion, publications have referred to the use of wet-and-dry bulbs for $H_2O$ determinations,[29] but our impression of such devices is that the results obtainable would be of dubious validity. We felt that, as an alternative, use of an efficient drying agent in solid form, such as Drierite or $Mg(ClO_4)_2$, would be preferable.

In accordance with the above viewpoint, we evaluated Drierite as a collector for water vapor. A tube packed with a weighed quantity of Drierite, approximately 50 g, was placed between the heated probe and the flow meter shown in either Figure 4 or 5, with all of the other components of the apparatus omitted. Experimental data obtained with simulated flue-gas mixtures showed high efficiency of water-vapor recovery and indicated that accurate determinations of water-vapor concentration could be made in the presence of other flue-gas components. Determinations of $H_2O$ vapor in field studies were, therefore, made on the basis of sample collection with Drierite.

### 4. Determination of NO and $NO_2$ in combination

Still other components of flue gases that may be indirectly involved in gas conditioning are the oxides of nitrogen, NO and $NO_2$. Occasional determinations were made of the sum of concentrations of these two oxides, referred to as $NO_x$. The procedure consisted of sample collection as $HNO_3$ in aqueous $H_2SO_4$, neutralization of the acidic sample with KOH, addition of phenoldisulfonic acid to produce nitrophenoldisulfonic acid, and spectrophotometric determination of the nitro compound.[21]

The results of all determinations of $NO_x$ are included in this report as a matter of record. No attempt was made, however, to draw any conclusions about the influence of $NO_x$ on fly-ash conditioning.

# III. STUDIES OF POWER PLANTS EQUIPPED WITH FACILITIES FOR THE INJECTION OF ANHYDROUS $SO_3$ VAPOR

## A. Cherokee Station, Unit 2

### 1. Description of the plant facilities

The Cherokee Station is operated by the Public Service Company of Colorado in Denver, Colorado. It consists of four units ranging in production capacity from 110 to 360 MW. Units 1, 2, and 4 are equipped with facilities for the injection of $SO_3$ from a central installation in which commercial stabilized $SO_3$ (obtained from Allied Chemical Corporation under the tradename "Sulfan") is converted from the liquid to the vapor in a stream of dry air.[30] The $SO_3$ injection facilities were designed and installed by Lodge-Cottrell Limited during the first part of 1971. As discussed in the following section, Unit 3 is equipped with an independent system for the injection of $H_2SO_4$ by evaporation of the concentrated acid.[30] Installation of the injection facilities at the four Cherokee units was made to cope with high resistivities—in excess of $1 \times 10^{11}$ ohm cm at temperatures of 290°F and above—that are typical of fly ash from the coal normally burned in the Cherokee Station (mined in Routt County, Colorado).

During this program, studies of the Cherokee system for $SO_3$ injection were made only at Unit 2. This unit, which has a rated capacity of 110 MW, includes both a mechanical collector and an electrostatic precipitator for fly-ash removal at temperatures averaging about 290°F. The $SO_3$ is pumped to the injection site at a concentration of about 9% by volume in air at an elevated temperature of undetermined value and injected through a manifold between the mechanical and electrostatic collectors.* This manifold consists of 42 injection lines inserted into the wall of the duct in a rectangular grid roughly 20 ft in the vertical direction (the direction of flow of the flue gases) and roughly 25 ft in the horizontal direction. Presumably, each injection line leads to a number of ports in a horizontal plane across the path of the flue gases, but the geometry of the injection system within the duct cannot be stated with certainty. Each of the injection lines is fitted with a valve that should permit uniform injection of the $SO_3$ if the opening of the valve is properly adjusted or, in other words, permit compensation for non-uniform flow of flue gases in various cross-sections of the duct.

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* The general characteristics of injection systems for $SO_3$ or Sulfan are discussed in detail in Section VIII.

Although the conditioning agent passes through the injection lines in dry air as $SO_3$ vapor, it must be rapidly and quantitatively converted to $H_2SO_4$ vapor on entering the duct, where it reacts with excess $H_2O$ vapor at a comparatively low temperature of 290°F. The injection system has sufficient capacity to produce an $H_2SO_4$ concentration in the duct in excess of 20 ppm by volume with the unit operating at full load, with flue gases being produced at the rate of about 500,000 $ft^3/min$ (here, the concentration and the flow rate are expressed on an actual basis—*i.e.*, with $H_2O$ vapor present at the nominal temperature of 290°F and the ambient pressure of 0.83 atm).

Our studies were made at Cherokee Unit 2 on July 6 and 7, 1971, soon after the injection system had been placed in operation and before the owner company had performed enough tests to realize optimum performance. At the time of our visit, the optimum rate of $SO_3$ injection was believed to be that used to produce 15 to 20 ppm of $H_2SO_4$ in the duct. However, this range now appears to be too high on the basis of the experimental data given in the following sections.

## 2. Results of conditioning studies

### a. Analyses of the coal

Composite samples of coal being fed to the boiler of Cherokee Unit 2 on July 6 and 7 were analyzed for total sulfur and ash. The results are listed in Table 4. The results for the two dates show good agreement in sulfur percentages but a substantial difference in ash percentages. The discrepancy in ash concentrations is of little concern, however, because most of the data relative to gas conditioning were taken on July 7.

The data for the coal sample collected on July 7 are representative values for coal from the source being used (Routt County, Colorado), based on analyses reported by the Bureau of Mines[31,32] and on our analysis from an investigation at Cherokee Unit 3 in October, 1970 (see Section IV.A.1).

Table 4. Sulfur and Ash Contents of Coal Burned at Cherokee Unit 2

| Component | Concentration, % July 6 | Concentration, % July 7 |
|---|---|---|
| Sulfur | 0.60 | 0.62 |
| Ash | 12.2 | 7.9 |

Most of the sulfur in Routt County coal is distributed between the pyritic and organic forms, as shown by the analyses given later. Data published by the Bureau of Mines and cited in Section IV.A.1 of this report show that strongly basic oxides, such as CaO, represent about 10% of the ash in Routt County coal, whereas the three most common weakly basic and acidic substances—$Al_2O_3$, $Fe_2O_3$, and $SiO_2$—represent about 80% of the ash in this coal.

### b. Resistivity of the fly ash

All of the resistivity data for Cherokee Unit 2 were taken on July 7 with the point-plane probe inserted in a port immediately ahead of the electrostatic precipitator.

Attempts to determine the resistivities of the initial series of collected samples with a high-voltage power supply, as described in Section II.B, were completely unsuccessful, in view of evident electrical breakdown in the collected samples at electric fields lower than 1.0 kV/cm. It was then learned that faulty combustion conditions in the boiler were producing an unusually high percentage of unburned carbon in the ash, of the order of 5% by weight rather than the usual 0.5% by weight or less. It was assumed that an even higher volume percentage of carbon in the ash (expected on the basis of reported differences in density of unburned carbon and fly ash)[33] must have existed and the large volume percentage of highly conductive carbon particles caused electrical breakdown at unusually low applied fields.

The only available means of overcoming the above difficulty was to use an electrometer (Keithley Model 610C) as both the voltage source and the current-measuring device. With this apparatus, the maximum applied voltage was only 0.01 kV and the maximum electric field produced in the samples was only of the order of 0.1 kV/cm or less. The resistivity data, therefore, cannot be directly compared with data from other plants, where resistivities are reported for substantially higher fields.

The resistivity data obtained without $SO_3$ injection and with $SO_3$ injection to produce estimated concentrations of 13 and 27 ppm in the duct are listed in Table 5. The concentrations of injected $SO_3$ were calculated from the evaporation rates of $SO_3$ and the flow rate of flue gases determined by the utility company during our study. Calculations from the available data led to results that were approximately 30% higher than the concentrations of 10 and 20 ppm originally requested before our experiments were started.

Despite the difficulties encountered in obtaining resistivity values under the desired conditions, the data nevertheless show that either concentration of injected $SO_3$ lowered the resistivity of the fly ash from a value in excess of $1 \times 10^{11}$ ohm to a value around $1 \times 10^{8}$ or less. There was no apparent gain in effectiveness of the conditioning agent on raising the concentration from 13 to 27 ppm. It is probable that even less than 5 ppm would have been entirely adequate for conditioning the ash to the extent required. It would obviously have been desirable to determine resistivity values at $SO_3$ concentrations below 13 ppm; however, it was not possible to make these determinations because a failure in the $SO_3$ injection system caused an extended interruption in its use.

Table 5. Electrical Resistivity of Fly Ash at Cherokee Unit 2

| Estimated concn of injected $SO_3$, ppm | Resistivity,[a] ohm cm |
|---|---|
| 0 | $1.6 \times 10^{11}$ |
| 13 | $1.4 \times 10^{7}$ |
| 13 | $5.6 \times 10^{7}$ |
| 27 | $2.5 \times 10^{7}$ |
| 27 | $3.8 \times 10^{7}$ |
| 27 | $5.0 \times 10^{7}$ |

---

a. Determined with the point-plane probe with an electric field of 0.1 kV/cm or less at a temperature of 290°F (July 7, 1971).

The effectiveness of the $SO_3$ for conditioning the ash was confirmed by readings of the secondary voltages and currents of the precipitator power supply. It was confirmed especially by a comparison of the voltages and currents in the power unit supplying the inlet section of the precipitator. With no injection, observed electrical values were 37 kV and 80 mA. With 27 ppm of injected $SO_3$, the corresponding set of electrical values was 41 kV and 720 mA. On injection of the conditioning agent, the spark rate in the inlet section decreased from 25 to 5 sparks/min.

### c. Chemical properties of the ash

Table 6 gives a summary of analytical data for individual fly-ash samples collected at the entrance of the electrostatic precipitator with the point-plane probe. This table also gives information about analytical properties of other ash samples collected with a cyclone device, one collected at the entrance of the precipitator and one collected near the entrance to the air heater (at a much higher temperature, upstream from the point of $SO_3$ injection). The column headings for the chemical properties are to be interpreted on the basis of information given in Section II.D. and in the footnote referring to the percentage of unburned carbon.

The following points are the most significant observations to be made:

- In the absence of any effect from injected $SO_3$ conditioning agent, the flow of the ash through the air heater and the mechanical collector caused

  —a decrease in pH from a moderately basic value (10.1) to an approximately neutral value (ca. 7)

  —an increase in the weight percentage of total sulfate from approximately 0.3 to 1.0%

  —an increase in weight percentage of free $H_2SO_4$ from about 0.01 to 0.05%

  —a reduction in the weight percentage of unburned carbon by about 11 to 4%.

  These effects must have resulted principally from the change in particle-size distribution that occurred during the loss of the larger particles in the mechanical collector. However, they may have resulted, in part, from interaction of the fly ash with the small concentration of naturally available $SO_3$, which was found at a concentration of 2 ppm ahead of the air heater (see the following section).

- With $SO_3$ injected at increasing levels, changes in the chemical properties of the ash consisted of

Table 6. Chemical Properties of Fly-Ash Samples Collected at Cherokee Unit 2

| Sampling location[a] | Temp, °F | Estimated concn of injected $SO_3$, ppm | Sample collector[b] | Concn of fly ash,[c] gr/ft$^3$ | Chemical properties of fly ash | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Soluble $SO_4^{-2}$, % | | |
| | | | | | pH | Total | $H_2SO_4$ | C,[d] % |
| AH | 695 | 0 | C | 2.60 | 10.1 | 0.29 | 0.01 | 11.1 |
| EP | 290 | 0 | P | 0.96 | 7.3 | 0.97 | 0.05 | 4.3 |
| EP | 290 | 0 | P | 0.96 | 6.6 | 1.28 | 0.05 | - |
| EP | 290 | 13 | P | 0.96 | 6.8 | 1.42 | 0.10 | - |
| EP | 290 | 13 | P | 0.96 | 6.9 | 1.51 | 0.10 | 4.4 |
| EP | 290 | 13 | C | 0.96 | 6.9 | 1.53 | - | 5.2 |
| EP | 290 | 27 | P | 0.96 | 7.1 | 1.85 | 0.19 | 3.5 |
| EP | 290 | 27 | P | 0.96 | 6.7 | 1.76 | 0.13 | - |
| EP | 290 | 27 | P | 0.96 | 7.4 | 1.89 | 0.11 | - |

---

a. AH signifies a location before the air heater, and EP signifies a location before the precipitator. The date of sampling was July 7, 1971.

b. C signifies a cyclone collector, and P signifies the point-plane probe.

c. Expressed for "standard" conditions—dry gases at 32°F and 1 atm. Values at the entrance to the precipitator are based on data obtained by the utility company on July 7. The value at the entrance to the air heater is estimated from a published correlation of ash concentrations in the coal and the dust,[34] although it is inconsistent with the utility company's estimate of an efficiency of 80% in ash removal in the mechanical collector

d. Determined on the basis of the quantity of $CO_2$ produced from unburned carbon particles in a C-H-N elemental analyzer.

—consistently increasing concentrations of total $SO_4^{-2}$

—generally increasing concentrations of free $H_2SO_4$.

The increases of about 0.4 and 0.8% in the $SO_4^{-2}$ content of fly ash at the ash concentration of 0.96 gr/ft$^3$ correspond to losses of about 1 and 2 ppm, respectively, in the injected concentrations of $SO_3$, which are small in comparison with original concentrations of 13 and 27 ppm, respectively.

### d. Concentrations of flue gases

Table 7 gives a summary of the observed concentrations of flue gases on two dates, July 6 and July 7. The principal observations to be made from the analytical data given in this table are as follows:

- The concentration of $H_2O$ was approximately constant, averaging 7.4% by volume.

- The concentration of $SO_3$ in the absence of injected conditioning agent ranged from 1 to 3 ppm. The lowest value, 1 ppm, was observed at the precipitator on July 6 when, unfortunately, no resistivity values could be obtained because of the previous described problem from unburned carbon in the ash. A somewhat higher value, 3 ppm, was observed at this location the next day; this value may not be as representative of the value normally to be found at this location, since it was not absolutely certain that the $SO_3$ injection line had cleared before sample was collected. It was necessary to collect the sample without injection on July 7 after all-day injection of $SO_3$; the time of sampling was deliberately delayed for nearly 1 hr after the injection equipment had been shut off. However, continued flow of air through the injection lines may have caused continued injection of $SO_3$ at a low level during the sampling, even though the plant personnel considered a delay of 1 hr sufficient. The value of 2 ppm ahead of the air heater on July 7 would not have been influenced by the injection of $SO_3$, which occurred at a location downstream from the air heater.

- Two results for the concentration of $SO_3$ during injection of the agent at the lower concentration (11 and

Table 7. Concentrations of Flue Gases at Cherokee Unit 2

| Date | Sampling location[a] | Temp, °F | Estimated concn of injected $SO_3$, ppm | Concentrations of flue gases[b] $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm |
|---|---|---|---|---|---|---|
| July 6 | EP | 290 | 0 | 7.3 | 1 | 432 |
| | EP | 290 | 0 | - | 1 | 422 |
| | EP | 290 | 0 | - | 1 | 406 |
| July 7 | AH | 695 | 0 | - | 2 | 507 |
| | AH | 695 | 0 | - | 2 | 512 |
| | EP | 290 | 0 | - | 3 | 473 |
| | EP | 290 | 13 | 7.4 | - | - |
| | EP | 290 | 13 | - | 12 | 452 |
| | EP | 290 | 13 | - | 11 | 442 |
| | EP | 290 | 27 | 7.5 | - | - |
| | EP | 290 | 27 | - | 26 | 460 |
| | EP | 290 | 27 | - | 23 | 420 |

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a. AH signifies a location before the air heater, and EP signifies a location before the precipitator.

b. The concentrations listed are the results of individual experiments and are expressed on the "wet" or actual basis. The concentration of $O_2$ recorded by the utility company was in the range from 4 to 5%.

12 ppm) were slightly below the estimated concentration of injected agent (13 ppm), as expected from the small amount of agent collected on the fly ash. The concentrations found during injection at the higher concentration (23 and 26 ppm) were also only slightly lower than the estimated concentration of injected agent (27 ppm), again as expected from the fly-ash analyses.

- The observed concentrations of $SO_2$ fluctuated through a range of nearly 100 ppm. The variations in $SO_2$ concentration are believed to reflect actual variations, primarily as a result of periodic variations in the composition of the coal being burned in the boiler. (Simultaneous determinations of $SO_2$ by our method and by either a similar method employed by other investigators or a method consisting of continuous instrumental monitoring leads to the conclusion that errors in our method would not be as large as 100 ppm in the 400 to 500 ppm range.)

As noted above, our data for $SO_3$ concentrations indicated that most of the injected $SO_3$ remained in the gas phase. Determinations of $SO_3$ at the precipitator outlet by chemists of the utility company confirmed that this phenomenon occurred. A concentration of 23 to 24 ppm was found at the outlet during injection of $SO_3$ at an estimated concentration of 27 ppm, confirming that an unnecessarily high concentration of $SO_3$ was injected. A lower, more acceptable emission of $SO_3$ would be expected with the injected concentration lowered, as seems desirable.

## B. X Station, Unit 4

### 1. Description of the power unit

The power station referred to by the code letter X cannot be identified by actual name or location in view of an agreement reached with the owner company. All of the information pertaining to this plant was provided by a representative of the company; none of the data given subsequently in this report was obtained by our staff and, thus, the reliability of the data cannot be vouched for. Of necessity, a full description of the plant cannot be given, but the most important features are described below.

The power unit of the X station discussed here employs only an electrostatic precipitator for the removal of fly ash. The operating temperature of the precipitator was reported to be 230°F during the tests with $SO_3$ injection. This temperature would normally be considered low enough for the $H_2O$ vapor in the flue gases to serve adequately by itself as a conditioning agent; however, the reported fly-ash resistivity of unconditioned ash at

230°F was 4.5 x $10^{11}$ ohm cm and thus above the desired maximum value of 2 x $10^{10}$ ohm cm.

Details of the $SO_3$ injection system were described only as follows: Sulfan was evaporated in a stream of preheated dried air with a temperature of 700°F and a dew point below -40°F, but it was injected in the duct at a much lower temperature of 300°F. Unquestionably, the $SO_3$ reacted with $H_2O$ vapor to produce $H_2SO_4$ vapor on entering the duct, and a large part of the $H_2SO_4$ may have condensed with additional $H_2O$ vapor to produce a mist of $H_2SO_4$ and $H_2O$ unless acid collection on the ash occurred at a faster rate than the condensation process (see Section VII.B.2).

### 2. Results of conditioning tests

Some of the results produced during the use of $SO_3$ as a conditioning agent are shown in Table 8. These are the only reported data showing the effects of $SO_3$; no information indicating changes in flue-gas composition was made available. However, it can be stated that the ash was treated with $SO_3$ at an unusually high concentration, 7.5 gr/$ft^3$ (expressed in terms of gas volume under standard rather than actual conditions of temperature and pressure) and, furthermore, the untreated ash was highly basic, producing a slurry pH of about 11 in an aqueous slurry. (The pH produced by a fly-ash sample from X station was determined in our laboratory by the usual procedure and found to be 11.7; we do not know, however, whether this sample was representative of the ash that was subjected to $SO_3$ conditioning.)

Table 8. Effects of $SO_3$ Conditioning Agent on the Resistivity and Sulfate Content of Fly Ash at X Station

| Injected concn of $SO_3$, ppm | Resistivity,[a] ohm cm | $SO_4^{-2}$, % |
|---|---|---|
| 0 | 4.5 x $10^{11}$ | 0.17 |
| 10 | 2.3 x $10^{10}$ | 0.31 |
| 18-20 | 7.0 x $10^{9}$ | 0.38 |

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[a] Determined with a point-plane apparatus at an unspecified electric field.

# IV. STUDIES OF POWER PLANTS EQUIPPED WITH FACILITIES FOR THE INJECTION OF VAPORS FROM LIQUID $H_2SO_4$

## A. Cherokee Station, Unit 3

### 1. Description of the plant facilities*

As previously stated, Unit 3 of the Cherokee Station, with a rated production capacity of 165 MW, has facilities for the injection of vapors from liquid $H_2SO_4$, whereas Units 1, 2, and 4 have a common $SO_3$ injection system.[30] The injection system was installed by Western Precipitator Division of Joy Manufacturing Company and placed in operation in August or September of 1970. As originally installed (and also as now operated), the system injected the acid vapors immediately ahead of the mechanical collector and thus subjected all of the fly ash from the boiler to conditioning, unlike the $SO_3$ system at Cherokee Unit 2. During November, 1970, however, the system was temporarily modified to inject the conditioning agent between the mechanical collector and the precipitator and thus treat only the relatively small fly-ash particles that cannot be removed mechanically. The temperature of flue gases through the mechanical and electrostatic collectors ranges from about 300 to 310°F.

The source of acid vapors in the Cherokee Unit 3 conditioning system is commercial 66°Bé $H_2SO_4$ (containing 93.2% of $H_2SO_4$ and 6.8% of $H_2O$ by weight[35]). The acid is evaporated in a stream of hot combustion gases that are produced by burning natural gas with sufficient excess air to produce the following approximate gas concentrations:[30] $CO_2$, 2%; $H_2O$, 5%; $O_2$, 16%; and $N_2$, 77%. Evaporation of the acid reportedly occurs within the temperature range of 700 to 1000°F,[30] which is high enough to decompose the $H_2SO_4$ extensively to $SO_3$ and $H_2O$ but to avoid decomposition of the $SO_3$ to $SO_2$ (see Section VIII.C).

The injection system includes a manifold of about 8 injection lines inserted into the duct at regular intervals in a line across the direction of flow of flue gases. The nature of the distribution system for injected vapors inside the duct is not known. The volume ratio of carrier gases for the conditioning agent to flue gases in the duct, however, is reportedly about 1:770.[30] Because the agent can be injected to produce a concentration of conditioning agent in the duct in excess of 40 ppm, the combined concentrations of $SO_3$ and $H_2SO_4$ in the injection lines must exceed 30,000 ppm on occasion. From considerations of the dew point of the $H_2O$-$SO_3$-$H_2SO_4$ mixture and the maximum absolute pressure in the injection line (approximately 0.98 atm) the temperature of the injection must be at least 400°F to avoid loss of conditioning agent by condensation before injection occurs (see Section VIII.C). Conversion of the $SO_3$ in the injection lines to $H_2SO_4$ presumably occurs rapidly following entrance into the duct, with an excess of $H_2O$ vapor and at a temperature of only 300 to 310°F.

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* Most of the descriptive information given here is based on published literature as cited, not on information disclosed by the utility company or the contractor for the injection facilities.

Our work on the site of Cherokee Unit 3 was performed during the period from October 13 to 19, 1970, when the acid vapors were injected ahead of the mechanical collector as at present. However, supplemental studies were conducted with samples collected by Public Service Company personnel both before and after the site of injection was moved temporarily to the duct between the mechanical and electrostatic collectors during the following month.

## 2. Results of conditioning studies

### a. Analyses of the coal

Table 9 gives the results of analyses of samples of the coal being fed to the boiler of Cherokee Unit 3 on October 17 and 19 when two series of determinations of fly-ash resistivity were made. This table indicates that the coal contained approximately 0.5% of sulfur and 8.6% of ash on both dates. The composition was only slightly different from the composition of coal from the same source (Routt County, Colorado) found at Cherokee Unit 2 on another occasion, as previously discussed in Section III.A.l.

Table 9. Sulfur and Ash Contents
of Coal Burned at Cherokee Unit 3

| Component | | Concentration, % | |
|---|---|---|---|
| | | October 17 | October 19 |
| Sulfur | | | |
| as sulfate | | 0.02 | 0.02 |
| as pyritic sulfur | | 0.12 | 0.23 |
| as organic sulfur | | 0.33 | 0.29 |
| | Total | 0.47 | 0.54 |
| Ash | | 8.72 | 8.57 |

Table 10 gives the concentrations of individual components of the ash sample prepared during the determination of the concentration of ash in the coal collected on October 19 and shows the high ratio of weakly basic and acid substances to strongly basic substances that is characteristic of Routt County coal. The data in Table 10 were determined by fusing the ash sample with $NaCO_3$; cooling the melt and neutralizing it with HCl; and analyzing the residue for $SiO_2$ gravimetrically,[36] $Fe_2O_3$ and CaO by titration procedures with EDTA,[37] MgO and $Al_2O_3$ by atomic absorption spectroscopy,[38] and $K_2O$ by flame photometry.[39]

Table 10. Components of the Ash in the Coal Burned at Cherokee Unit 3

| Component | Concentration, % |
|---|---|
| $SiO_2$ | 45.4 |
| $Al_2O_3$ | 30.0 |
| $Fe_2O_3$ | 5.4 |
| CaO | 7.3 |
| MgO | 2.6 |
| $K_2O$ | 1.1 |
| Subtotal[a] | 91.8 |

---

a. Other components would include $SO_3$ and numerous relatively minor components such as $TiO_2$, $P_2O_5$, and $Na_2O$.

b. Resistivity of the fly ash

Resistivities of fly ash at the entrance of the precipitator at Cherokee Unit 3 were determined on two dates, October 17 and 19. In the first series of measurements, a mixture of coal and natural gas was used as the fuel in the boiler, with the natural gas representing about 25% of the fuel value. In the second series of measurements, only coal was used as the fuel.

Determinations of resistivity were made with the two types of cyclone probes described in Section II.B with an average electric field of 2.0 to 2.5 kV/cm in each sample. Data were obtained both with and without $H_2SO_4$ injection, with concentrations of the conditioning agent reportedly as high as 33 and 44 ppm during the two series of determinations.

Table 11 summarizes the results of the resistivity determinations. This table shows that surprisingly little change in resistivity was produced during the injection of $H_2SO_4$. In either series of measurements, the largest reduction observed was less than one order of magnitude, despite the high concentrations of $H_2SO_4$ that were reportedly injected.

Table 11. Electrical Resistivity
of Fly Ash at Cherokee Unit 3
(Validity questionable as discussed in text)

| Date[a] | Temp, °F | Reported concn of injected $H_2SO_4$, ppm | Resistivity,[b] ohm cm |
|---|---|---|---|
| Oct. 17 | 300 | 0 | $2.0 \times 10^{12}$ |
| | | 6 | $9.3 \times 10^{11}$ |
| | | 17 | $7.8 \times 10^{11}$ |
| | | 26 | $5.6 \times 10^{11}$ |
| | | 33 | $5.0 \times 10^{11}$ |
| Oct. 19 | 310 | 0 | $1.0 \times 10^{12}$ |
| | | 13 | $1.0 \times 10^{12}$ |
| | | 26 | $6.0 \times 10^{11}$ |
| | | 33 | $6.3 \times 10^{11}$ |
| | | 44 | $6.6 \times 10^{11}$ |

---

a. On October 17, a mixture of coal and natural gas was used as the fuel. On October 19, only coal was used as the fuel.

b. Determined with cyclone probes with an average electric field of 2.0 to 2.5 kV/cm.

### c. Chemical properties of ash samples collected from the ducts ahead of the air heater and the precipitator

Table 12 lists the results of chemical analyses of fly-ash samples collected with cyclone probes in sampling ports ahead of the air heater and ahead of the electrostatic precipitator during conditioning tests with coal only as the fuel.

The data obtained in the absence of conditioning agent show evidence of a reduction in the basicity of the ash and an increase in the sulfate content of the ash as the sampling point was moved from the location ahead of the air heater to the location ahead of the precipitator. As at Cherokee Unit 2, these changes must

## Table 12. Chemical Properties of Fly-Ash Samples Collected from Ducts at Cherokee Unit 3

| Sampling location[a] | Temp, °F | Reported concn of injected $H_2SO_4$, ppm | Concn of fly ash,[b] gr/ft³ | Median particle size, µm | Chemical properties of fly ash | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | pH | Soluble base as CaO, % | Soluble $SO_4^{-2}$, % | |
| | | | | | | | Total | $H_2SO_4$[c] |
| AH | 740 | 0 | 2.6 | 2.0 | 10.5 | 0.65 | 0.57 | - |
| EP | 310 | 0 | 0.4 | 1.5 | 10.0 | 0.35 | 0.77 | 0.01 |
| EP | 310 | 13 | 0.4 | 1.5 | 9.9 | 0.34 | 0.90 | - |
| EP | 310 | 26 | 0.4 | 1.5 | 9.9 | 0.31 | 1.09 | - |
| EP | 310 | 33 | 0.4 | 1.5 | 9.8 | 0.28 | 1.00 | - |
| EP | 310 | 44 | 0.4 | 1.5 | 9.5 | 0.25 | 1.12 | 0.02 |

---

a. AH signifies a location before the air heater, and EP signifies a location before the precipitator. The date of sampling was October 19, 1970, with coal alone as the fuel. Cyclone probes were used as the sample collectors.

b. Expressed for "standard" conditions. Estimated at the air heater from the ash content of the coal and at the precipitator from data supplied by the utility company.

c. Determined after several months of sample storage in the laboratory and thus perhaps lower than those immediately after collection.

have been the result principally of a change in particle-size distribution across the mechanical collector; however, they may have been caused, in part, by interaction of the fly ash with $SO_3$ to convert part of the basic components of the ash to the corresponding $SO_4^{-2}$ salts.

The data obtained at the precipitator with and without injection of the conditioning agent show further decreases in the basicity of the ash and increases in the $SO_4^{-2}$ content as the concentration of the conditioning agent was increased, indicating that the ash collected at least part of the conditioning agent, even though only small reductions in resistivity were observed as a result.

### d. Concentrations of flue gases

Table 13 gives the results of flue-gas analyses with and without injection of conditioning agent during the tests with both coal and natural gas as fuels and with only coal as the fuel.

The data in Table 13 that are of primary interest are the concentrations of $SO_3$. With up to 33 or 44 ppm of the conditioning agent added, increases of only 1 to 2 ppm of $SO_3$ were observed. These very small changes are in marked contrast to the large changes observed at Cherokee Unit 2 during $SO_3$ injection.

The other data in Table 13 require only brief comment. The $SO_2$ concentration was only about 220 during burning of both coal and gas and about 350 ppm during burning of coal alone. This difference is attributable to the low concentration of $SO_2$ produced from natural gas. The value of 350 ppm is about 100 ppm lower than the typical value observed at Cherokee Unit 2 with Routt County coal, containing a slightly higher percentage of sulfur.

It is of interest to compare the amounts of conditioning agent reportedly injected with the amounts accounted for by the fly-ash and flue-gas analyses. Under the conditions with 44 ppm reportedly injected, the quantity of $SO_4^{-2}$ gained by the ash at the entrance to the precipitator was 0.35% (Table 12). If it is assumed that all of the ash exposed to the conditioning agent (ca. 2.6 gr/ft$^3$) gained the same amount of sulfate, the quantity of conditioning agent accounted for on the ash by a gain of 0.35% is approximately 5 ppm. Combination of this value with the gain in $SO_3$ found in the gas phase, approximately 2 ppm, gives a total of only 7 ppm, less than 20% of the concentration reportedly injected. In contrast, the results obtained at Cherokee Unit 2 accounted for essentially 100% of each concentration of $SO_3$ injected.

## Table 13. Concentrations of Flue Gases at Cherokee Unit 3

| Date[a] | Sampling location[b] | Temp, °F | Reported concn of injected $H_2SO_4$, ppm | Concentrations of flue gases[c] | | | |
|---|---|---|---|---|---|---|---|
| | | | | $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm | $NO_x$, ppm |
| Oct. 13 | AH | 740 | 0 | - | 2 | 226 | - |
| Oct. 17 | EP | 300 | 0 | 9.5 | <1 | 222 | 415 |
| | | | 6 | - | <1 | 222 | - |
| | | | 17 | - | <1 | 210 | - |
| | | | 26 | - | <1 | 217 | - |
| | | | 33 | - | 2 | 216 | - |
| Oct. 16 | AH | 740 | 0 | - | <1 | 314 | - |
| Oct. 19 | EP | 310 | 0 | - | 1 | 358 | - |
| | | | 13 | 7.7 | 1 | 357 | 392 |
| | | | 26 | - | <1 | 349 | - |
| | | | 33 | - | 2 | 349 | - |
| | | | 44 | 8.4 | 3 | 357 | - |

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a. On October 13 and 17, a mixture of coal and natural gas was burned in the boiler. On October 16 and 19, only coal was used as the fuel.

b. AH signifies a location before the air heater, and EP signifies a location before the precipitator.

c. Expressed on the "wet" or actual basis. The concentration of $O_2$ recorded by the utility company was in the range from 3 to 4%.

### e. Chemical properties of ash samples collected from the hoppers of the mechanical collector and the electrostatic precipitator

In view of the discrepancies between injected concentrations of the conditioning agent and calculated concentrations based on changes in fly-ash and flue-gas compositions, it was of interest to determine whether the fly ash deposited in the mechanical collector collected a disproportionately high concentration of the conditioning agent. Unfortunately, no sample of ash deposited in the mechanical collector was collected during our visit to Cherokee Unit 3 during October. In the absence of these samples, we requested personnel of the utility company to remove samples from the hoppers of the mechanical collector at a later date and to submit these samples for analysis along with samples collected simultaneously from the hoppers of the electrostatic precipitator. Two groups of samples were thus obtained; two sets were collected during continued injection of $H_2SO_4$ ahead of the mechanical collector and one set was collected during injection between the mechanical and electrostatic collectors. The results of the analyses are listed in Table 14.

Table 14. Chemical Properties of Fly-Ash Samples from Hoppers at Cherokee Unit 3

| | | | Chemical properties of fly ash | | |
|---|---|---|---|---|---|
| Date[a] | Reported concn of injected $H_2SO_4$, ppm | Hopper location[b] | pH | Soluble base as CaO, % | Soluble $SO_4^{-2}$ (total), % |
| Nov. 17 | 0 | MC | 11.1 | 1.51 | 0.33 |
| | 40 | MC | 10.7 | 0.73 | 0.72 |
| | 0 | EP | 9.9 | 0.51 | 1.58 |
| | 40 | EP | 9.1 | 0.17 | 1.96 |
| Nov. 18 | 0 | MC | 10.8 | 0.79 | 0.20 |
| | 50 | MC | 10.6 | 0.59 | 0.41 |
| | 0 | EP | 9.4 | 0.20 | 1.04 |
| | 50 | EP | 9.7 | 0.31 | 1.00 |
| Nov. 23 | 0 | MC | 11.1 | 1.17 | 0.16 |
| | 15 | MC | 11.3 | 1.45 | 0.23 |
| | 0 | EP | 10.3 | 0.48 | 0.87 |
| | 15 | EP | 10.4 | 0.56 | 0.87 |

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[a] On November 17 and 18, acid injection occurred ahead of the mechanical collector. On November 23, it occurred between the mechanical and electrostatic collectors.

[b] MC signifies the mechanical collector; EP signifies the electrostatic precipitator.

The data for samples exposed to the conditioning agent ahead of the mechanical collector on November 17 and 18 lead to conflicting observations. On the first occasion, the ash deposited mechanically gained less sulfate during $H_2SO_4$ injection than that deposited electrostatically; on the second occasion, the ash in the hoppers of the mechanical collector showed a slight gain in sulfate during injection, whereas that in the hoppers of the electrostatic precipitator showed a small decrease or, practically speaking, no change of real significance. If it is assumed that the ash deposited in the mechanical collector on November 17 and 18 corresponded to a concentration in the inlet duct of 2.2 gr/ft$^3$ (an estimate corresponding to the concentrations previously listed), the gains in $SO_4^{-2}$ correspond to concentrations of conditioning agent of only 1 to 2 ppm, a negligible fraction of the 50 ppm that was reportedly injected.

The data for samples collected on November 23 with injection between the mechanical and electrostatic collectors show, practically speaking, no gain of sulfate in the ash deposited mechanically (as expected) or in the ash deposited electrostatically (contrary to the expected result), despite the fact that 15 ppm was reportedly injected to condition fly ash at an estimated concentration of only 0.4 gr/ft$^3$.

Unfortunately, no data on fly-ash resistivity or flue-gas composition are available for the dates on which the hopper samples were collected. The gain in $SO_4^{-2}$ content of ash collected electrostatically on November 17 suggests that little change in resistivity was effected, because this gain was about the same as that observed with little change in resistivity on October 19 (Table 12). The absence of measurable increases in the $SO_4^{-2}$ content on either November 18 or 23 implies that no change in resistivity was effected on these dates. It seems reasonable to assume that negligible increases in the concentration of $SO_3$ in the gas phase occurred on any of the dates in November—especially on either of the latter two occasions—in view of the fact that our work in various plants has never shown a measurable increase in the concentration of $SO_3$ during injection of conditioning agent without a measurable increase in the $SO_4^{-2}$ content of fly ash.

## B. Arapahoe Station, Unit 4

### 1. Description of the plant facilities

The Arapahoe Station is the second of two stations in Denver that are operated with $SO_3$ or $H_2SO_4$ injection systems. Originally, only Unit 4 was equipped with acid injection facilities, and this unit was investigated by our staff on October 21 and 22, 1970, shortly after the installation of the injection facilities was completed by the contractor, Universal Oil Products Company. In the first half of 1971, however, the acid evaporation system was enlarged and additional injection lines were installed to permit acid injection in Units 2 and 3. The remaining unit at Arapahoe, Unit 1, is now consistently operated with natural gas as the fuel and thus is not serviced by the present injection system.

Low-sulfur coals from Weld County, Colorado, and Hanna County, Wyoming, are usually used as fuels in Arapahoe Units 2, 3, and 4. They produce fly ash of high resistivity, as typified by our observed value of $3.8 \times 10^{12}$ ohm cm with unconditioned ash from Weld County coal at a temperature of 275°F. Acid conditioning was considered to be the most expedient solution to the high-resistivity problem at Arapahoe as at Cherokee.

Owing to a secrecy agreement between the Public Service Company and Universal Oil Products Company, a complete description of the acid injection system used at Arapahoe Unit 4 during our field studies cannot be given in this report. The following, however, can be stated: The source of the acid vapors was 66°Bé $H_2SO_4$, the carrier gas for the acid vapors from the evaporator was air with ambient relative humidity, the acid was evaporated at a lower temperature than at Cherokee Unit 3, and the site of injection was the duct between the mechanical and electrostatic precipitators. The acid vapors could be injected in the duct at a sufficient rate to produce concentrations in the duct above 20 ppm (as $H_2SO_4$) with the unit at full load, 110 MW, and producing flue gases at a total rate of about 525,000 $ft^3$/min at 275°F and ambient pressure, approximately 0.83 atm.

## 2. Results of conditioning studies

### a. Analyses of the coal

Analytical results for the coal from Weld County, Colorado, that was burned during the conditioning studies at Arapahoe Unit 4, are shown in Tables 15 and 16. The sulfur and ash contents given in Table 15 are similar to those of Routt County coal, which were previously given in Tables 4 and 8 in connection with studies at Cherokee Units 2 and 3. The composition of the ash in the Weld County coal given in Table 16 is substantially different from that in the Routt County coal, which was previously given in Table 10. The most significant differences are that the Weld County coal contains higher percentages of strongly basic oxides, such as CaO, and lower percentages of weakly basic or acidic oxides, such as $SiO_2$ and $Al_2O_3$. The observed differences are consistent with differences in the compositions reported by the U. S. Bureau of Mines.[31,32]

Table 15. Sulfur and Ash Contents of Coal Burned at Arapahoe Unit 4

| Component | Concentration, % |
|---|---|
| Sulfur | |
| as sulfate | 0.02 |
| as pyritic sulfur | 0.06 |
| as organic sulfur | 0.41 |
| Total | 0.49 |
| Ash | 5.87 |

Table 16. Components of the Ash in the Coal Burned at Arapahoe Unit 4

| Component | Concentration, % |
|---|---|
| $SiO_2$ | 36.1 |
| $Al_2O_3$ | 19.0 |
| $Fe_2O_3$ | 7.3 |
| CaO | 15.6 |
| MgO | 4.2 |
| $K_2O$ | 0.8 |
| Subtotal[a] | 83.0 |

---

[a] Other components would include $SO_3$ and numerous relatively minor components such as $TiO_2$, $P_2O_5$, and $Na_2O$.

b. Resistivity of the fly ash

Data showing resistivity values of the fly ash at Arapahoe Unit 4 are listed in Table 17. These data were obtained with a cyclone probe in which an average electric field of 2.0 to 2.5 kV/cm was imposed on each collected sample. The data indicate that the resistivity was lowered by nearly two orders of magnitude with only 6 ppm of injected $H_2SO_4$ and by only slightly higher degrees with 12 or 18 ppm of the conditioning agent.

c. Chemical properties of the fly ash

Observed properties of fly-ash samples collected in cyclone probes in the ducts ahead of the mechanical collector and the

Table 17. Electrical Resistivity of Fly Ash at Arapahoe Unit 4

| Reported concn of injected $H_2SO_4$, ppm | Resistivity,[a] ohm cm |
|---|---|
| 0 | $3.8 \times 10^{12}$ |
| 6 | $5.7 \times 10^{10}$ |
| 12 | $3.2 \times 10^{10}$ |
| 18 | $1.9 \times 10^{10}$ |

---

[a] Determined with a cyclone probe with an average electric field of 2.0 to 2.5 kV/cm at a temperature of about 275°F (October 21 or 22, 1970).

electrostatic precipitator are listed in Table 18. In comparison with data previously given for Cherokee Units 2 and 3, the data in Table 18 indicate that the fly ash at Arapahoe was appreciably more basic than that at the Cherokee Units and was more comparable in basicity to the ash at X station. The only evidence that the available base was neutralized by the conditioning agent was found with the highest injected concentration of $H_2SO_4$, 18 ppm. Yet, on the other hand, the $SO_4^{-2}$ content of the ash increased consistently as the injected concentration of $H_2SO_4$ increased.

A possible explanation for relatively constant values of pH and concentrations of soluble base, despite increasing concentrations of $SO_4^{-2}$, is that the fly ash contained enough base in excess of the collected $H_2SO_4$ to saturate the aqueous phase of the slurry at the concentration of 3%. In other words, it is possible that all of the base did not dissolve with the proportions of ash and water used.

The high basicity of the Arapahoe ash compared with the properties of the Cherokee ash are consistent with the marked differences in CaO concentrations of the ash fractions noted previously in discussions of the different coals burned at the two plants.

### d. Concentrations of flue gases

Concentrations of flue gases found at Arapahoe Unit 4 are listed in Table 19. The data of primary interest—the concentrations of $SO_3$—show a maximum increase of 2 ppm with 18 ppm of

Table 18. Chemical Properties of Fly-Ash Samples Collected at Arapahoe Unit 4

| Sampling location[a] | Temp, °F | Reported concn of injected $H_2SO_4$, ppm | Concn of fly ash,[b] gr/ft³ | Median particle size, µm | Chemical properties of fly ash | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | pH | Soluble base as CaO, % | Soluble $SO_4^{-2}$, % Total | Soluble $SO_4^{-2}$, % $H_2SO_4$ |
| AH | 740 | 0 | 2.3 | 1.7 | 11.1 | 1.93 | 1.00 | - |
| EP | 275 | 0 | 0.5 | 1.5 | 11.1 | 2.10 | 1.50 | nil[c] |
| EP | 275 | 6 | 0.5 | 1.5 | 11.1 | 2.10 | 2.23 | - |
| EP | 275 | 12 | 0.5 | 1.5 | 11.0 | 2.14 | 2.50 | - |
| EP | 275 | 18 | 0.5 | 1.5 | 10.8 | 1.62 | 2.97 | nil[c] |

---

a. AH signifies a location before the air heater, and EP signifies a location before the precipitator. The dates of sampling were October 21 and 22, 1970. Cyclone probes were used as the sample collectors.

b. Expressed for "standard" conditions. Estimated at the air heater from the ash content of the coal and at the precipitator from data supplied by the utility company.

c. Reported as "nil" in view of the absence of a pH change in an ethanol-water slurry. Determined after several months of storage in the laboratory and thus not necessarily representative of the value at the time of sample collection.

Table 19. Concentrations of Flue Gases at Arapahoe Unit 4

| Sampling location[a] | Temp, °F | Reported concn of injected $H_2SO_4$, ppm | Concentrations of flue gases[b] | | | |
|---|---|---|---|---|---|---|
| | | | $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm | $NO_x$, ppm |
| AH | 740 | 0 | - | <1 | 416 | - |
| EP | 275 | 0 | 8.9 | <1 | 387 | - |
| EP | 275 | 6 | - | 1 | 446 | - |
| EP | 275 | 12 | 8.8 | 2 | 413 | - |
| EP | 275 | 18 | - | 2 | 430 | 626 |

---

a. AH signifies a location before the air heater, and EP signifies a location before the precipitator. The dates of sampling were October 21 and 22, 1970.

b. Expressed on the "wet" or actual basis. The concentration of $O_2$ recorded by the utility company was usually in the range from 4 to 5%.

$H_2SO_4$ injected. This increase is comparable to that found at Cherokee Unit 3 with 44 ppm of $H_2O$ reportedly injected but much lower than that to be expected at Cherokee Unit 2 with 18 ppm of $SO_3$ injected, based on data at higher and lower concentrations of $SO_3$.

It is of interest to compare the concentrations of $H_2SO_4$ reported injected at Arapahoe Unit 4 with the sums of the concentrations found as increases in the $SO_4^{-2}$ content of the fly ash and increases in the $SO_3$ content of the gas phase. Table 20 lists data permitting this comparison, assuming that fly ash entering the precipitator at an estimated concentration of 0.5 gr/ft$^3$ uniformly increased in $SO_4^{-2}$ content by the percentages indicated in Table 18. The comparison shows that, of the reported concentration of injected $H_2SO_4$, the percentage accounted for ranged from 33 to 50%, substantially higher than the value calculated for Cherokee Unit 3 (20%) but lower than the values observed at Cherokee Unit 2 (essentially 100%).

Table 20. Reported Concentrations of Injected $H_2SO_4$ and Equivalent Observed Concentrations in the Fly Ash and Flue Gases at Arapahoe Unit 4

| Reported concn of injected $H_2SO_4$, ppm | Calculated concn based on sample analyses, ppm | | |
|---|---|---|---|
| | Fly ash | Flue Gases | Total |
| 6 | 2 | 1 | 3 |
| 12 | 3 | 2 | 5 |
| 18 | 4 | 2 | 6 |

## C. Y Station, Unit 6

### 1. Description of the plant facilities

The Y Station, like the X Station previously discussed, cannot be identified by actual name, location, or owner company. However, the information presented here about the Y Station—unlike that pertaining to the X Station—was obtained during an on-site investigation by our staff and during subsequent laboratory analyses of samples collected at the plant.

The Y Station has a rated power-production capacity of about 140 MW. It is equipped only with an electrostatic precipitator for the removal of fly ash, and the operating temperature of the precipitator is approximately 320°F. The vapors from concentrated $H_2SO_4$ are injected in the duct entering the precipitator through a grid of 24 uniformly-spaced injection ports that are located in a plane across the path of flow of flue gases; each of the injection ports is an open 0.125-in. pipe and is fed with conditioning agent through a series of branched injection lines that originate at a central acid evaporator.

The contractor that installed the injection system cannot be identified by name in this report. However, the basic features of the injection system can be described in fairly specific terms as follows: The source of the acid vapors is 66°Bé $H_2SO_4$, and the production of the vapors occurs with co-current flows of the liquid acid and preheated ambient air through a bed in which the maximum inlet-air temperature is about 500°F and the minimum outlet-gas temperature is about 400°F. Thus, the injection system operates at substantially lower temperatures than that at Cherokee Unit 3; it is of the type referred to as a "low-temperature" $H_2SO_4$ system and discussed in Section VIII. The acid vapors pass through the injection lines principally as $H_2SO_4$; the balance present as $SO_3$ presumably reacts rapidly with excess $H_2O$ vapor to produce additional $H_2SO_4$ on entering the duct and cooling to 320°F.

The fairly simple geometry of the duct between the injection ports and the sampling ports for fly-ash and flue-gas samples at the Y Station permitted a reasonably accurate estimate of the contact time of the conditioning agent and the fly ash between injection and sampling. In some of the experiments with the power unit operating a full load, the contact time was about 1 sec; in other experiments with the unit at half load, the contact time was approximately 2 sec. The contact time of 1 sec was probably the minimum in all of the plants investigated, although the contact times in the other plants could not, as a rule, be estimated with comparable accuracy.

The capacity of the $H_2SO_4$ evaporator limited the injected concentration of conditioning agent to a value of 8 ppm with the boiler at full load, producing a flow of flue gas of approximately 500,000 $ft^3$/min (expressed on the basis of water present for the temperature of 320°F and the ambient pressure of approximately 1 atm). With the $H_2SO_4$ operating at full capacity and the boiler at half load, however, an injected concentration of 16 ppm was reached during some of our experiments.

## 2. Results of conditioning studies

### a. Analyses of the coal

The results of analyses of coal samples collected on the two dates of our investigation at the Y station (March 1 and 2, 1971) are given in Table 21. The data in this table indicate that the sulfur percentage averaged about 0.6% and the ash percentage averaged about 12% and did not differ appreciably on the two dates.

Table 21. Sulfur and Ash Contents of Coal Burned at Y Station

| Component | Concentration, % |  |
|---|---|---|
|  | March 1 | March 2 |
| Sulfur | 0.64 | 0.59 |
| Ash | 12.34 | 11.34 |

No effort was made to determine the distribution of sulfur in various forms or to determine the composition of the ash. Other data obtained during analyses of the fly ash produced in the absence of conditioning agent indicated, however, that the ash was virtually neutral in terms of the relative concentrations of soluble bases and acids.

### b. Resistivity of the fly ash

Fly-ash samples to be used for determinations of electrical resistivity were collected at the entrance of the electrostatic precipitator with two devices, the cyclone and point-plane probes described in Section II.B. The electric field during all of the measurements with the cyclone sampler was 2.5 kV/cm. The electric field during various measurements with the point-plane sampler, on the other hand, varied from 2.1 to 3.7 kV/cm. This variation was the result of applying a voltage of either 0.1 or 0.5 kV across samples that ranged in thickness from 0.04 to 0.23 cm in thickness.

The data given in Table 22 indicate that the injection of either 4 or 8 ppm of $H_2SO_4$ vapor lowered the resistivity from $2 \times 10^{12}$ ohm cm to about $1 \times 10^{11}$ ohm cm and that injection of 16 ppm caused further lowering to values in the approximate range from $1 \times 10^{9}$ to $1 \times 10^{10}$ ohm cm. It is not known why 4 and 8 ppm of the conditioning agent produced about the same resistivity change; it is possible that the explanation lies in the fact that experiments with 4 ppm were carried out one day and the other experiments with 0, 8, 16 ppm were carried out the following day (the coal analyses for the two days of experimentation do not give much basis for this hypothesis, however). The data obtained with the cyclone and point-plane probes were in good agreement for 4 and 8 ppm of conditioning agent but differed by roughly a factor of 10 with 16 ppm injected. The disparity in the data at 16 ppm may have been the result, in part, of an average higher electric field in the point-plane samples (3.4 kV/cm, compared with 2.5 kV/cm in the cyclone samples).

Table 22. Electrical Resistivity of Fly Ash at Y Station

| Reported concn of injected $H_2SO_4$, ppm | Sampling device[a] | Electric field, kV/cm | Resistivity,[b] ohm cm |
|---|---|---|---|
| 0 | C | 2.5 | $2.0 \times 10^{12}$ |
| | C | 2.5 | $2.0 \times 10^{12}$ |
| 4 | C | 2.5 | $1.2 \times 10^{11}$ |
| | P | 2.9 | $0.7 \times 10^{11}$ |
| | C | 2.5 | $1.8 \times 10^{11}$ |
| | P | 2.4 | $2.0 \times 10^{11}$ |
| | C | 2.5 | $1.5 \times 10^{11}$ |
| 8 | P | 2.8 | $1.4 \times 10^{11}$ |
| | C | 2.5 | $1.3 \times 10^{11}$ |
| | P | 2.1 | $2.1 \times 10^{11}$ |
| | C | 2.5 | $1.6 \times 10^{11}$ |
| 16 | P | 3.1[c] | $1.1 \times 10^{10}$ |
| | C | 2.5 | $0.1 \times 10^{10}$ |
| | P | 3.7[c] | $2.5 \times 10^{10}$ |
| | C | 2.3 | $0.2 \times 10^{10}$ |

---

a. C and P indicate cyclone and point-plane sampling probes, respectively.

b. Determined with different resistivity probes and slightly varying fields, as indicated by second and third columns, at a temperature of 320°F. Listed in the sequence as actually determined with 8 ppm of $H_2SO_4$ on March 1 and with 0, 4, or 16 ppm of $H_2SO_4$ on March 2.

c. In excess of 3.0kV/cm and thus in excess of any of the other electric fields, simply as a result of the thickness of the sample collected and the voltage applied across the sample.

### c. Chemical properties of the fly ash

Table 23 summarizes the data showing the chemical properties of the fly ash collected by different methods both in the absence and presence of conditioning agent.

Table 23. Chemical Properties of Fly-Ash Samples Collected at Y Station

| Sampling location[a] | Temp °F | Reported concn of injected $H_2SO_4$, ppm | Sampling device[b] | Chemical properties[c] of fly ash | | | |
|---|---|---|---|---|---|---|---|
| | | | | pH | | Soluble $SO_4^{-2}$, % | |
| | | | | Min. | Eq'm. | Total | $H_2SO_4$ |
| AH | >600 | 0 | F | -[d] | 6.9 | 0.27 | - |
| EP | 320 | 0 | C | -[d] | 8.1 | 0.24 | <0.01 |
| | | 4 | C | 4.7 | 5.7 | 0.35 | - |
| | | | P | 4.6 | 6.5 | 0.29 | - |
| | | 8 | C | 4.5 | 4.6 | 0.41 | - |
| | | | P | 4.6 | 5.6 | 0.34 | - |
| | | 16 | C | 4.4 | 4.6 | 0.36 | 0.01 |
| | | | P | 4.1 | 4.2 | 0.51 | - |

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a. AH signifies a location before the air heater, and EP signifies a location before the precipitator. The dates of sampling were March 1 and 2, 1971. Both cyclone and point-plane probes were used for collecting samples, as indicated by the fourth column.

b. F designates a filtration unit employed by the personnel of the station, whereas C and P indicate cyclone and point-plane resistivity probes.

c. Estimated concentration was 3.3 gr/ft$^3$ (standard conditions). Number median diameter was *ca*. 2.0 µm.

d. No minimum was observed; the recorded value increased continuously toward equilibrium value.

One of the most notable features of the analytical data is that the pH values indicate that the fly ash was essentially neutral in the absence of conditioning agent but became distinctly acidic in the presence of the conditioning agent. Minima in the pH values observed during equilibration of samples with water gave evidence of a strong-acid layer overlying less acidic or slightly basic substances in the water-soluble surface layers. Determinations of $H_2SO_4$ on two samples approximately 3 months after the samples were collected gave further evidence that the conditioning agent produced an $H_2SO_4$-containing outer layer on the fly-ash particles.

Another feature of the analytical data is that the maximum gain in $SO_4^{-2}$ caused by the conditioning agent was only about 0.25% of the fly-ash weight. Unfortunately, the $SO_4^{-2}$ data do not show a consistent trend toward higher values as the concentration of conditioning agent was increased. Our failure to observe the expected trend is attributed, in part, to variations in the $SO_4^{-2}$ percentage in unconditioned ash and, in part, to differences in sampling properties of the cyclone and point-plane probes.

### d. Concentrations of flue gases

Table 24 summarizes the results of determinations of the concentrations of $H_2O$, $SO_3$, and $SO_2$ in the flue gases. The $H_2O$ and $SO_2$ values are all in the expected range and show significant variations only in the $SO_2$ concentrations, which indicate that a possible hour-to-hour variation of significant magnitude occurred in the sulfur content of the coal. The $SO_3$ data show that less than 1 ppm of $SO_3$ was present until conditioning agent was injected and then the concentration of $SO_3$ increased sharply and represented most of the injected agent at each level of injection. The discrepancy in the two concentrations, 6 and 11 ppm, found with 8 ppm injected was larger than expected; it is not known whether the discrepancy was the result of experimental error or poor control of the injection rate.

Table 24. Concentrations of Flue Gases at Y Station

| Reported concn of injected $H_2SO_4$, ppm | Concentrations of flue gases[a] | | |
|---|---|---|---|
| | $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm |
| 0 | 7.7 | <1 | 373 |
| | | <1 | 384 |
| 4 | 7.3 | - | 397 |
| | | 4 | 391 |
| 8 | 7.7 | 6 | 391 |
| | | 11 | 475 |
| 16 | 7.9 | 14 | 488 |
| | | 12 | 470 |

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a. Determined at the entrance to the electrostatic precipitator. Expressed on the "wet" or actual basis.

## V. STUDY OF A POWER PLANT EQUIPPED WITH FACILITIES FOR INJECTION OF ANHYDROUS $NH_3$ VAPOR

### A. Description of the Widows Creek Station, Unit 7

The Widows Creek Station is one of several power stations in the Tennessee Valley Authority System that burns coal of unusually high sulfur content—about 3.5%, on the average. In such power plants, problems in precipitator performance from high-resistivity ash is not to be expected because of the abundance of naturally produced $SO_3$; in several of the plants, nevertheless, poor precipitator performance is encountered. Data published by Reese and Greco[11] indicate that the low-resistivity of the ash and accompanying excessive reentrainment is the principal cause of difficulty.

The injection of $NH_3$ has been found a promising means of improving precipitator performance at Unit 7 of the Widows Creek plant. Widows Creek Unit 7 was built with a production capacity of about 575 MW and only an electrostatic precipitator for the removal of fly ash. Several years ago, however, the plant was modified by installation of facilities to permit $NH_3$ injection ahead of the air heater on one side of the dual system of ducts leading from the boiler to the precipitator; later, because of difficulties from air-heater clogging, the injection facilities were modified to provide injection between the heater and the entrance of the precipitator.[11] The injection system is quite simple; it consists only of a lance with several openings into the duct; the simplicity of design permits periodic removal of the injection line from the duct and cleaning of solid deposits from the lance as necessary. The modified system was operated intermittently during several visits by our staff to the Widows Creek plant, including a visit on April 5 and 6, 1971, that is discussed in detail in this report.

One of our objectives in visits to the Widows Creek plant was to study conditioning by the abundant naturally occurring $SO_3$ in a range of temperatures. Unit 7 is designed in such a manner that the temperature in one of the ducts leading to the precipitator can be raised or lowered from the normal temperature of about 270°F with a corresponding temperature change in the opposite direction in the second duct. The second objective was to gain an understanding of the mechanism of $NH_3$ conditioning under the conditions that prevail at Widows Creek Unit 7. Several hypotheses to explain the effect have been advanced; in general, these hypotheses are based on assumptions that the $NH_3$ acts as a base to neutralize part of the $SO_3$, thus raising the inherently low fly-ash resistivity and minimizing reentrainment, especially that occurring during the rapping of collector electrodes to deposit the collected ash in the precipitator hoppers.[11] Thus, the mechanism of $NH_3$ conditioning at Widows Creek is distinctly different from that in other plants referred to in Section I, where the function of $NH_3$ is to overcome high resistivity.

## B. Analyses of Coal Samples

On April 5 and 6, 1971, studies were made at Widows Creek Unit 7 both with and without $NH_3$ injection. A number of coal samples were collected at intervals on these two dates in April and analyzed separately for sulfur and ash. Both sulfur and ash concentrations were reasonably constant throughout the sampling period but were found to range from 3.31 to 3.74% and from 16.0 to 19.0%, respectively. The average concentrations of 3.59% of sulfur and 17.5% of ash appeared to be fairly representative of the fuel throughout the period of conditioning studies as well as during normal periods of operation of the plant, in view of coal analyses supplied by TVA personnel.

No attempt was made to determine the different forms of sulfur and the components of the ash during the work in April. However, determinations on another occasion indicate that approximately 75% of the sulfur is pyritic and most of the balance is organic. Moreover, pH determinations of aqueous slurries of the fly ash collected on different occasions indicate that the ash is normally rich in soluble basic substances.

## C. Investigation of Conditioning in the Absence of $NH_3$ Conditioning Agent

### 1. Resistivity of the fly ash

Table 25 lists the results of determinations of the fly-ash resistivity at recorded temperatures ranging from 254 to 288°F—below and above the normal value of 270°F. These data in this table were obtained with both cyclone and point-plane probes with the usual electric field of 2.5 kV/cm in the cyclone samples and various electric fields in the range from 0.6 to 15.0 kV/cm in the point-plane samples. At least two determinations were made with different electric fields in each point-plane sample, and up to nine determinations were made with different fields in selected samples. The data obtained for the point-plane samples at various fields were plotted in a graph; interpolations and extrapolations from this graph were made to permit reporting of the values of resistivity at electric fields of 1.0, 2.5, 5.0, and 10 kV/cm.

Table 25. Electrical Resistivity of Fly Ash at Widows Creek Unit 7 without $NH_3$ Conditioning[a]

| Temp, °F | Resistivity, ohm cm, found with different sample collectors and various electric fields | | | | |
|---|---|---|---|---|---|
| | Cyclone collector, 2.5 kV/cm | Point-plane collector | | | |
| | | 1.0 kV/cm | 2.5 kV/cm | 5.0 kV/cm | 10.0 kV/cm |
| 288 | - | $7.0 \times 10^{10}$ | $2.6 \times 10^{10}$ | $1.0 \times 10^{10}$ | $0.5 \times 10^{10}$ |
| 286 | $7.5 \times 10^{9}$ | $1.0 \times 10^{11}$ | $4.5 \times 10^{10}$ | $1.7 \times 10^{10}$ | $0.3 \times 10^{10}$ |
| 284 | $1.0 \times 10^{10}$ | - | - | - | - |
| 258 | - | $5.0 \times 10^{8}$ | $3.7 \times 10^{8}$ | $2.8 \times 10^{8}$ | $2.2 \times 10^{8}$ |
| 254 | $1.0 \times 10^{9}$ | - | - | - | - |

---

a. Determined on April 5 and 6, 1971.

Based on a comparison of data at an electric field of 2.5 kV/cm, the resistivity of fly ash at the Widows Creek plant appeared to decrease from about $1 \times 10^{10}$ ohm cm or more at temperatures near 285°F to about $1 \times 10^{9}$ ohm cm or less at temperatures near 255°F. Thus, the resistivity at the normal operating temperature of about 270°F would be well below the assumed maximum value of $2 \times 10^{10}$ ohm cm for efficient precipitator operation. The decrease in resistivity of about one order of magnitude during a reduction of temperature of 30°F in the range below 300°F is at least qualitatively in agreement with the trend in resistivity described by White;[1] it signifies the increasing surface conduction by collected vapors—assumed to be principally $H_2O$—as the temperature is lowered.

## 2. Chemical composition of the fly ash

Table 26 shows the results of chemical analyses of four of the six fly-ash samples for which resistivity data were given in the preceding section. No result is given for the remaining two samples, which were lost on removing the point-plane probe from the duct. Also, no comparative data for samples collected ahead of the air heater can be reported; during the work at the Widows Creek plant in April, no apparatus was available for collection of fly ash through the small sampling ports that were available ahead of the air heater.

Table 26. Chemical Properties of Fly-Ash Samples Collected Ahead of the Electrostatic Precipitator at Widows Creek Unit 7 without $NH_3$ Conditioning[a]

| Temp, °F | Sampling device[b] | Chemical properties[c] of fly ash | | |
|---|---|---|---|---|
| | | | Soluble $SO_4^{-2}$, % | |
| | | pH | Total | $H_2SO_4$ |
| 286 | C | 11.0 | 0.73 | 0.04 |
| 286 | P | 10.8 | 0.79 | - |
| 284 | C | 11.0 | 0.77 | - |
| 254 | C | 10.7 | 0.88 | - |

---

a. Determined on April 5 and 6, 1971.

b. C and P indicate cyclone and point-plane sampling probes, respectively.

c. Estimated concentration was 4.1 gr/ft$^3$ (standard conditions).

The analyses of fly-ash samples collected at temperatures near 285 and 255°F at the entrance of the precipitator indicate that a slight increase in the $SO_4^{-2}$ content of the ash—approximately 0.1%—occurred as the temperature was lowered. It appears, therefore, that the lowering of resistivity was caused not only by increased collection of $H_2O$ vapor but also by increased collection of $SO_3$ vapor or, more exactly, $H_2SO_4$ vapor in view of the range of temperatures studied.

## 3. Concentrations of flue gases

Concentrations of $H_2O$, $SO_3$, and $SO_2$ found in the ducts ahead of the air heater and the precipitator are listed in Table 27. These concentrations show much higher values of both of the sulfur oxides than the values found in other plants previously discussed, in which coals of much lower sulfur contents were burned.

The $SO_3$ concentrations, in particular, show that substantial concentrations of this conditioning agent are naturally available when a high-sulfur coal is burned as at the Widows Creek plant. The $SO_3$ concentrations also show the decrease expected with decreasing temperature and increased collection on the fly ash.

Table 27. Concentrations of Flue Gases at Widows Creek Unit 7 without $NH_3$ Conditioning

| Sampling location[a] | Temp, °F | Concentrations of flue gases[b] | | |
|---|---|---|---|---|
| | | $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm |
| AH | 625 | - | 15 | 2860 |
| | | | 20 | 2460 |
| EP | 288 | - | 15 | 2660 |
| | 286 | 7.9 | - | 2640 |
| | 284 | - | 18 | 2640 |
| | 254 | - | 8 | 2450 |

---

a. AH signifies a location before the air heater, and EP signifies a location before the precipitator. The dates of sampling were April 5 and 6, 1971.

b. Expressed on the "wet" or actual basis. The concentration of $O_2$ recorded by the utility company was approximately 3%.

## D. Investigation of Conditioning with Injected $NH_3$

### 1. Resistivity of the fly ash

During the studies on April 5 and 6, $NH_3$ was injected at rates calculated to produce concentrations of 7 and 15 ppm of $NH_3$ vapor in the duct between the air heater and the electrostatic precipitator. During injections of $NH_3$ at the 7-ppm level, duct temperatures were near 275°F; during injections at the 15-ppm level, duct temperatures were near 285°F during one series of experiments and near 255°F during a second series of experiments. The results of resistivity determinations during injections of $NH_3$, determined by the same procedures as those used in the absence of $NH_3$, are listed in Table 28.

All of the resistivity values obtained at an electric field of 2.5 kV/cm, both with and without $NH_3$ injection, are plotted in Figure 6 to show possible effects of $NH_3$ injection. Graphs A and B in this figure show cyclone and point-plane data separately; however, in both graphs the same line is used to show approximate averages from the two sets of data. In general, the plotted data show little evidence of an effect of $NH_3$ on resistivity. The strongest indication of an effect from $NH_3$ is given by the point-plane data at temperatures in the range from 280 to 290°F. Here, the apparent effect is a slight lowering of resistivity, and this effect is contrary to the expected increase in resistivity. It is our opinion that the available resistivity data cannot explain the improvement in precipitator efficiency that injected $NH_3$ reportedly produces at the Widows Creek plant.

Table 28. Electrical Resistivity of Fly Ash at Widows Creek Unit 7 with $NH_3$ Conditioning[a]

| | Resistivity, ohm cm, found with different sample collectors and various electric fields | | | | |
|---|---|---|---|---|---|
| | Cyclone collector, | Point-plane collector | | | |
| Temp, °F | 2.5 kV/cm | 1.0 kV/cm | 2.5 kV/cm | 5.0 kV/cm | 10.0 kV/cm |
| 278 | $2.3 \times 10^9$ | $4.5 \times 10^9$ | $2.8 \times 10^9$ | $1.6 \times 10^9$ | $0.8 \times 10^9$ |
| 274 | - | $4.5 \times 10^9$ | $2.8 \times 10^9$ | $1.6 \times 10^9$ | $0.8 \times 10^9$ |
| 273 | $3.0 \times 10^9$ | - | - | - | - |
| 290 | $7.5 \times 10^9$ | - | - | - | - |
| 289 | - | $1.3 \times 10^{10}$ | $5.8 \times 10^9$ | $3.0 \times 10^9$ | $1.0 \times 10^9$ |
| 286 | - | $3.3 \times 10^{10}$ | $1.4 \times 10^{10}$ | $7.5 \times 10^9$ | $2.5 \times 10^9$ |
| 283 | $5.0 \times 10^9$ | $6.0 \times 10^9$ | $2.2 \times 10^9$ | $0.9 \times 10^9$ | $0.5 \times 10^9$ |
| 256 | $2.5 \times 10^9$ | $2.8 \times 10^8$ | $2.1 \times 10^8$ | $1.6 \times 10^8$ | $1.3 \times 10^8$ |

---

[a] Determined on April 5 and 6, 1971, with 7 ppm injected at temperatures of 273-278°F and with 15 ppm injected at temperatures of 256 and 283-290°F.

2. Chemical properties of the fly ash

Table 29 summarizes the results of chemical analyses of some of the samples collected for resistivity determinations. Unfortunately, data cannot be given for several samples collected with the point-plane apparatus, because loss of these samples occurred as the collecting device was being removed from the duct. Table 29 includes the results not only of pH and $SO_4^{-2}$ determinations but the results of $NH_3$ determinations for three samples. Determinations of the $NH_3$ extracted in aqueous slurries were made by use of Nessler's reagent.[40] Control experiments with known amounts of $NH_3$ added to extracts of unconditioned ash showed that at least 60 to 80% of the $NH_3$ to be expected on conditioned ash could be found, assuming quantitative collection of the conditioning agent. With 15 ppm of $NH_3$ injected and collected on the ash, the concentration of $NH_3$ in a sample of the ash would be 0.12% by weight; with 7 ppm injected, the concentration would be 0.05%.

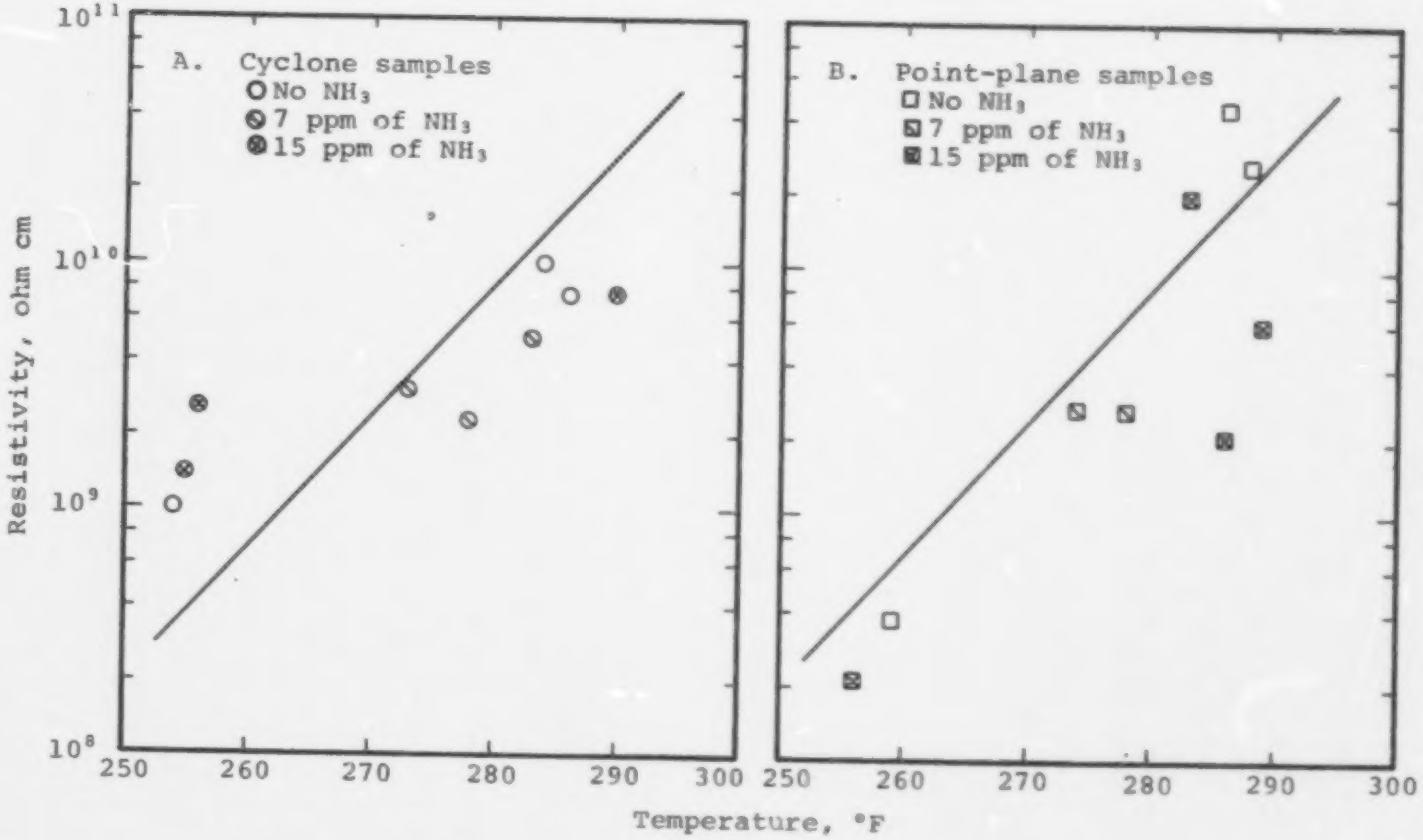

Figure 6. Resistivity of Fly Ash at Widows Creek Unit 7 with and without $NH_3$ Injection

Table 29. Chemical Properties of Fly-Ash Samples Collected Ahead of the Electrostatic Precipitator at Widows Creek Unit 7 with $NH_3$ Conditioning[a]

| Calculated concn of $NH_3$, ppm | Temp, °F | Sampling device[b] | Chemical properties of fly ash | | | |
|---|---|---|---|---|---|---|
| | | | | Soluble $SO_4^{-2}$, % | | |
| | | | pH | Total | $H_2SO_4$ | Soluble $NH_3$, % |
| 7 | 278 | C | 11.4 | 0.94 | 0.04 | <0.02 |
| | 278 | P | 10.5 | 1.15 | - | - |
| | 274 | P | 11.0 | 1.29 | - | <0.02 |
| | 273 | C | 11.4 | 0.87 | - | - |
| 15 | 290 | C | 11.6 | 0.94 | - | - |
| | 283 | C | 11.6 | 1.03 | 0.04 | <0.02 |
| | 256 | C | 10.9 | 0.86 | - | - |
| | 256 | P | 9.5 | 1.21 | - | - |

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a. Determined on April 5 and 6, 1971.

b. C and P indicate cyclone and point-plane sampling probes, respectively.

c. Estimated concentration was 4.1 $gr/ft^3$ (standard conditions).

The data in Table 29 show marked disparities in the pH and $SO_4^{-2}$ data for cyclone and point-plane samples at either rate of $NH_3$ injection or at any of the experimental temperatures. In general, the data indicate that more $SO_3$ was collected by the point-plane apparatus than by the cyclone collector, a phenomenon apparent in studies at some of the other plants.

The data showing $SO_4^{-2}$ concentrations in the ash with and without $NH_3$ injection (Tables 26 and 29) are plotted for comparison in Figure 7. The line constructed in this figure shows the expected concentrations of $SO_4^{-2}$ at various temperatures, based on the estimated fly-ash concentration (4.1 $gr/ft^3$) and on the observed $SO_3$ concentrations at various temperatures (summarized subsequently in Figure 8). The line in Figure 7 has a negative slope corresponding to the positive slope of the relationship between the concentration of $SO_3$ and the temperature. There is unfortunate scatter in the data about the line in Figure 7. However, despite the scatter, it appears reasonable to draw the conclusion that a change in temperature had a greater influence than the injection of $NH_3$ on the $SO_4^{-2}$ concentration in the ash.

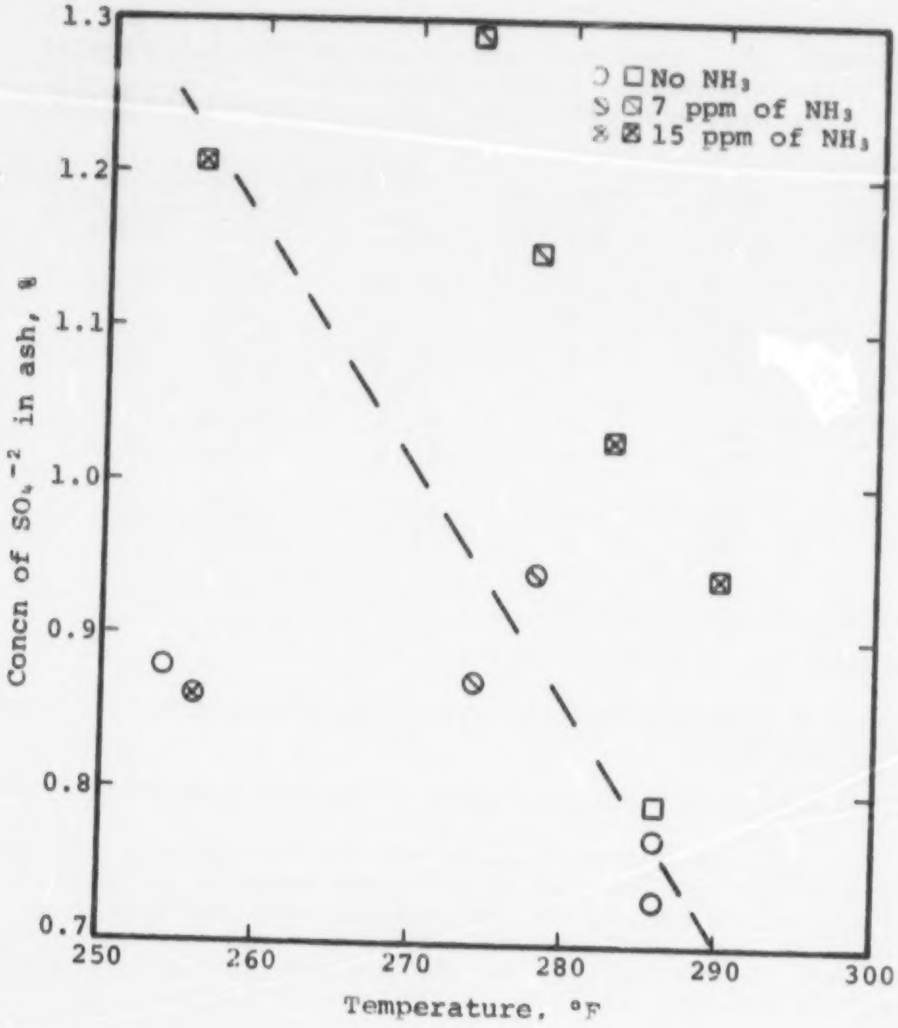

Figure 7. Concentration of $SO_4^{-2}$ in Fly Ash at Widows Creek Unit 7 with and without $NH_3$ Injection
(Circles represent data for samples collected in a cyclone probe, whereas squares represent data for samples collected in a point-plane probe. The line is discussed in the text.)

The results of $NH_3$ determinations showed no evidence of the presence of $NH_3$ on the ash. The sensitivity of the analytical method, however, was such that each result can be expressed only as a value less than 0.02% of the weight of the sample analyzed. On this basis, the results signify that less than 40% of the $NH_3$ injected at 7 ppm was found and less than 20% injected at 15 ppm was found.

In addition to the determinations of $NH_3$ in the fly-ash samples collected for resistivity determinations, still other determinations were made with samples collected on the quartz-wool particulate filter of the $SO_3$-$SO_2$ sampling train. The latter determinations led to the finding of the equivalent of about 4 ppm of $NH_3$ as the vapor at either level of injection. It appears that the $NH_3$ may have been present in the form of very small particles that were inefficiently collected by the cyclone and point-plane probes. The particulate matter may have been small fly-ash particles with a surface deposit of $NH_3$ or small particles of a reaction product between $NH_3$ and $H_2SO_4$ vapors, such as the $(NH_4)_2SO_4$ postulated by Reese and Greco.[11] It is also possible that $NH_3$ may have been sampled from the duct as a gas but retained on the glass wool or collected fly-ash particles by a process of adsorption.

## 3. Concentrations of flue gases

Concentrations of $H_2O$, $SO_3$, $SO_2$, and $NH_3$ in the flue gases during periods of $NH_3$ injection were determined, as shown by the experimental results in Table 30. For collecting $NH_3$ from the gas phase, a sampling train consisting of a heated probe and particulate filter (as described in Section II.E.) and a bubbler filled with 0.1 N aqueous $H_2SO_4$ was used; for determining the $NH_3$ collected in the $H_2SO_4$ solution, a procedure based on Nessler's reagent[40] was followed.

The concentrations of $H_2O$, $SO_3$, and $SO_2$ are similar to those found without $NH_3$ injection (Table 27). The concentrations of $NH_3$ represent only small fractions of the concentrations reportedly injected and are not large enough to account for the total concentrations reported when combined with the equivalent concentrations found in samples of the fly ash.

Table 30. Concentrations of Flue Gases at Widows Creek Unit 7 with $NH_3$ Conditioning[a]

| Calculated concn of injected $NH_3$, ppm | Temp, °F | Concentrations of flue gases[b] | | | |
|---|---|---|---|---|---|
| | | $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm | $NH_3$, ppm |
| 7 | 278 | 8.0 | 13 | 2620 | - |
| | 276 | - | - | - | 0.2 |
| | 274 | - | 15 | 2720 | - |
| | 273 | - | 13 | 2670 | - |
| 15 | 290 | - | 18 | 2850 | - |
| | 283 | 8.4 | - | - | 0.4 |
| | 254 | - | 10 | 2790 | - |

---

a. Collected at the entrance of the electrostatic precipitator on April 5 and 6, 1971.

b. Expressed on the "wet" or actual basis. The concentration of $O_2$ recorded by the utility company was approximately 3%.

The concentrations of $SO_3$ found with and without $NH_3$ injection are plotted in Figure 8. There is no apparent evidence of a significant change in the $SO_3$ during $NH_3$ injection, because the data points lie near Line A in the figure whether they were obtained with injection or without. If the injected $NH_3$ had reacted with $SO_3$ at concentrations indicated by Line A to produce particles of $(NH_4)_2SO_4$, the injection of 7 ppm of $NH_3$ would have lowered the $SO_3$ concentrations to values along Line B, and the injection of 15 ppm would have lowered the $SO_3$ concentrations to values along Line C. The inadequacy of either Line B or Line C for showing the observed concentrations of $SO_3$ with $NH_3$ injected indicates that reaction to produce $(NH_4)_2SO_4$ did not occur to a significant degree.

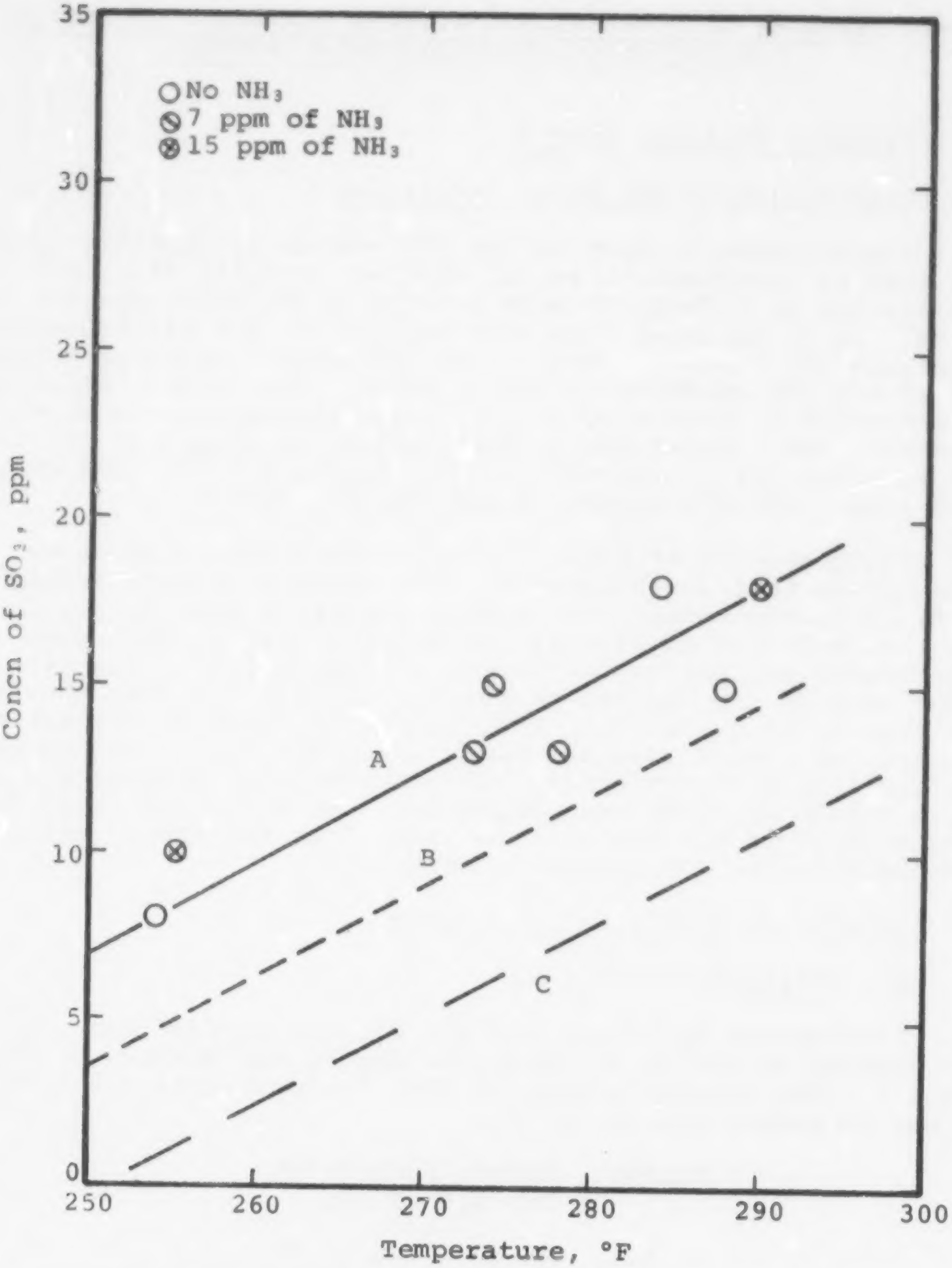

Figure 8. Concentrations of $SO_3$ Observed at Widows Creek Unit 7 with and without $NH_3$ Injection (Lines A, B, and C are discussed in the text.)

# VI. STUDIES OF POWER PLANTS WITHOUT PERMANENT FACILITIES FOR INJECTION OF CONDITIONING AGENTS

## A. Kingston Station, Unit 5

### 1. Description of the plant facilities

The Kingston Station in the TVA system is normally operated with coal of intermediate sulfur content, roughly 2%. Unit 5 of this station is a facility with a rated production capacity of 200 MW. It is equipped with both mechanical and electrostatic collectors for fly-ash removal, and the usual operating temperature of the precipitator is about 300°F. Even with a moderate concentration of naturally produced $SO_3$ available as a conditioning agent, the temperature is high enough to cause the fly ash to have an undesirably high resistivity (above $1 \times 10^{11}$ ohm cm), which lowers the efficiency of the precipitator.

Field studies at Kingston Unit 5 were conducted on two occasions during this investigation. The results of work on May 4, 5, and 6, 1971, are summarized in this report in detail, for they show the variation of fly-ash resistivity over a wide range in temperatures and corresponding $SO_3$ concentrations. The results of the work during May are of further interest in that they show the lowering of resistivity that can be effected by the use of $H_2O$ vapor as a conditioning agent. Kingston Unit 5 has no permanent facilities for injecting $H_2O$; however, for a brief period in May, a stream of water was pumped into the boiler to raise the concentration of $H_2O$ in the flue gases from the normal value of 7% to about twice the normal value or 14%.

### 2. Results of conditioning studies

#### a. Analyses of the coal

Percentages of sulfur and ash were determined for eight coal samples collected at intervals during the studies on May 4, 5, and 6. The results appear to vary randomly with sampling time and may be summarized as follows:

Sulfur: Range, 1.85-2.34%
Average, 2.12%

Ash: Range, 16.4-25.5%
Average, 19.6%

### b. Resistivity of the fly ash

Samples of fly ash to be used for determinations of electrical resistivity were collected at the entrance of the precipitator at Kingston Unit 5 with both cyclone and point-plane sampling probes. Results of the determinations of resistivity with an electric field of 2.5 kV/cm in the cyclone samples and electric fields of 1.0, 2.5, 5.0, and 10.0 kV/cm in the point-plane samples are listed in Table 31. Data obtained at a field of 2.5 kV/cm in both types of samples are plotted in Figure 9.

Table 31. Electrical Resistivity of
Fly Ash at Kingston Unit 5[a]

| Temp, °F | Resistivity, ohm cm, found with different sample collectors and various electric fields | | | | |
|---|---|---|---|---|---|
| | Cyclone collector, 2.5 kV/cm | Point-plane collector | | | |
| | | 1.0 kV/cm | 2.5 kV/cm | 5.0 kV/cm | 10.0 kV/cm |
| 372 | - | $1.7 \times 10^{12}$ | $1.4 \times 10^{12}$ | $1.0 \times 10^{12}$ | $7.0 \times 10^{11}$ |
| 370 | - | $2.7 \times 10^{12}$ | $1.8 \times 10^{12}$ | $1.3 \times 10^{12}$ | $1.0 \times 10^{12}$ |
| 365 | $3.6 \times 10^{12}$ | - | - | - | - |
| 350 | - | $2.0 \times 10^{12}$ | $1.3 \times 10^{12}$ | $1.0 \times 10^{12}$ | $7.0 \times 10^{11}$ |
| 347 | $1.7 \times 10^{13}$ | - | - | - | - |
| 346 | - | $6.6 \times 10^{11}$ | $5.8 \times 10^{11}$ | $4.6 \times 10^{11}$ | $3.6 \times 10^{11}$ |
| 341 | $2.0 \times 10^{13}$ | - | - | - | - |
| 329 | - | $1.3 \times 10^{12}$ | $9.0 \times 10^{11}$ | $6.0 \times 10^{11}$ | $4.0 \times 10^{11}$ |
| 328 | - | $7.8 \times 10^{11}$ | $6.0 \times 10^{11}$ | $4.2 \times 10^{11}$ | $3.0 \times 10^{11}$ |
| 325 | $3.0 \times 10^{12}$ | - | - | - | - |
| 323 | - | $2.8 \times 10^{12}$ | $1.6 \times 10^{12}$ | - | - |
| 323 | - | $2.1 \times 10^{12}$ | $1.7 \times 10^{12}$ | $1.1 \times 10^{12}$ | - |
| 319 | $3.3 \times 10^{12}$ | - | - | - | - |
| 308 | $1.7 \times 10^{12}$ | - | - | - | - |
| 302 | - | $2.6 \times 10^{11}$ | $2.1 \times 10^{11}$ | $1.5 \times 10^{11}$ | $1.1 \times 10^{11}$ |
| 301 | - | $2.9 \times 10^{11}$ | $2.3 \times 10^{11}$ | $1.7 \times 10^{11}$ | $1.2 \times 10^{11}$ |
| 296 | $5.5 \times 10^{11}$ | - | - | - | - |
| | | | | | |
| 335 | - | $4.0 \times 10^{11}$ | $3.2 \times 10^{11}$ | $2.3 \times 10^{11}$ | - |
| 331 | - | $1.8 \times 10^{11}$ | $1.5 \times 10^{11}$ | $1.1 \times 10^{11}$ | $8.8 \times 10^{10}$ |
| 329 | $2.0 \times 10^{11}$ | - | - | - | - |
| 323 | $1.5 \times 10^{11}$ | - | - | - | - |

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a. Determined on May 4, 5, and 6 without injection of $H_2O$ (first group of data) or with injection of $H_2O$ (second group of data).

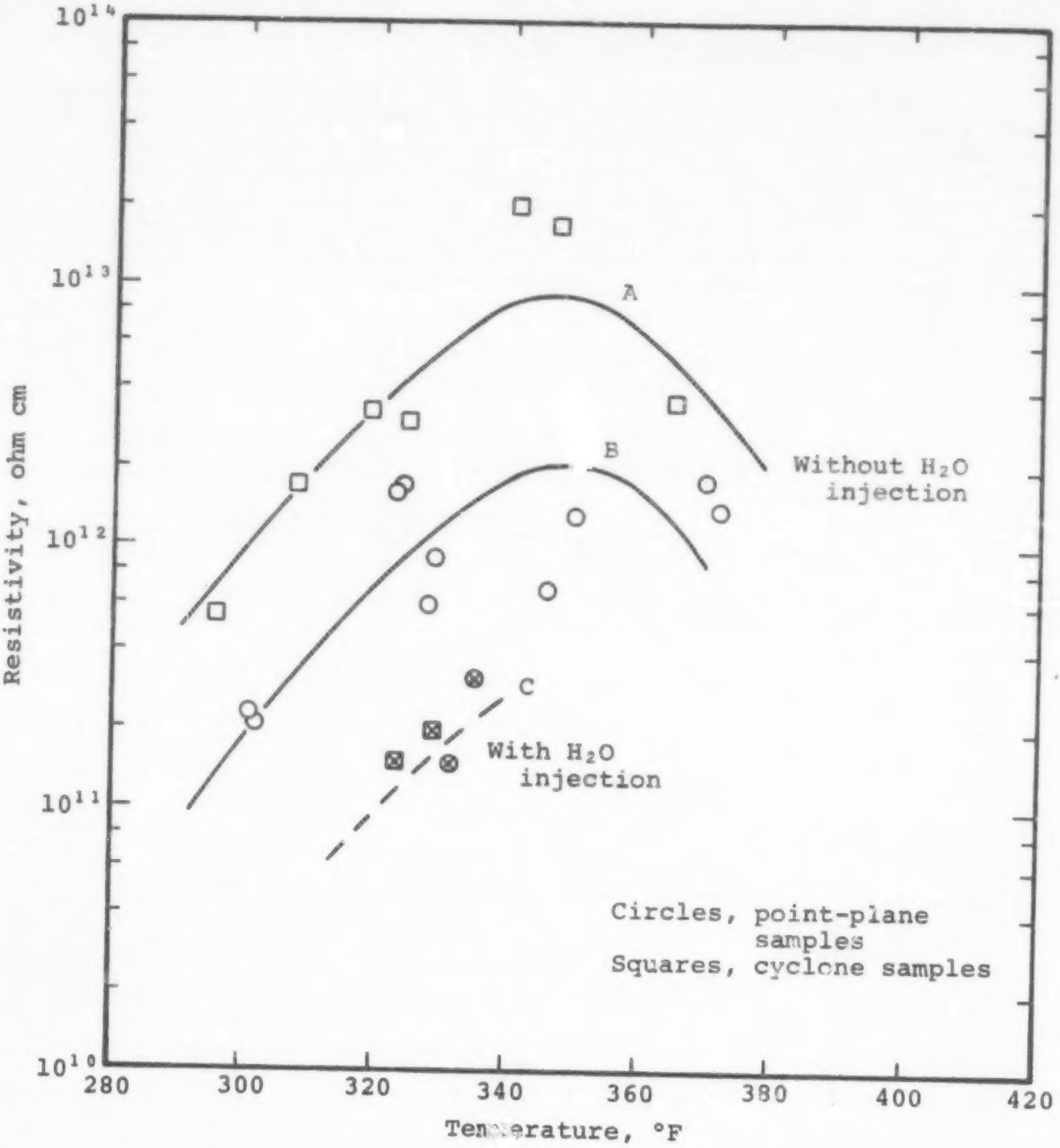

Figure 9. Electrical Resistivity of Fly Ash at Kingston Unit 5 with and without $H_2O$ Injection

The principal observations to be made from the data as plotted in Figure 9 are as follows:

- Resistivity values obtained in the absence of injected $H_2O$ with the cyclone apparatus are, on the average, nearly one order of magnitude higher than the values obtained with the point-plane apparatus, as indicated by Curves A and B. However, the data obtained during $H_2O$ injection are virtually the same with both devices.
- As the temperature was increased from the normal value of about 300°F, the resistivity increased to a maximum near 350°F and then decreased, as a result first of decreasing surface conduction and then increasing volume conduction, as described by White.[1] Obviously, lowering the temperature from 300°F would have produced a desirable reduction in resistivity, as a result of increased surface conduction.
- Injection of $H_2O$ to increase the vapor concentration from 7 to 14% lowered the resistivity at temperatures in the 320-340°F range by one to two orders of magnitude, depending upon the type of resistivity apparatus.

### c. Chemical properties of the fly ash

Table 32 lists the results of chemical analyses of fly-ash samples collected at Kingston Unit 5. Figure 10 shows graphs of the pH and $SO_4^{-2}$ values as functions of temperature.

One of the noteworthy aspects of the experimental results is that in the absence of injected $H_2O$ the fly ash was virtually neutral as collected at the high temperature of 645°F ahead of the air heater and then increasingly acidic as collected at decreasing temperatures in the range from 372 to 296°F ahead of the precipitator. A second noteworthy aspect of the data is that three of the four samples collected in the presence of injected $H_2O$ showed marked decreases in pH and increases in $SO_4^{-2}$ content in comparison with samples collected in the absence of injected $H_2O$ in the same temperature range. It is evident, therefore, that the effects of $H_2O$ injection on the ash included a marked increase in the collection of the available $SO_3$ by the fly ash.

### Table 32. Chemical Properties of Fly-Ash Samples Collected at Kingston Unit 5[a]

| Estimated concn of injected $H_2O$, % | Sampling location[b] | Temp, °F | Sampling device[c] | Chemical properties pH | Chemical properties Soluble $SO_4^{-2}$ (total), % |
|---|---|---|---|---|---|
| 0 | AH | 645 | C | 6.35 | 0.24 |
| | AH | 645 | C | 6.40 | 0.31 |
| 0 | EP | 372 | P | 6.38 | 0.32 |
| | EP | 370 | P | - | - |
| | EP | 365 | C | 5.77 | 0.34 |
| | EP | 350 | P | 6.60 | 0.33 |
| | EP | 347 | C | 6.57 | 0.35 |
| | EP | 346 | P | 6.09 | 0.40 |
| | EP | 341 | C | 6.07 | 0.38 |
| | EP | 329 | P | - | - |
| | EP | 328 | P | 5.70 | 0.34 |
| | EP | 325 | C | 4.87 | 0.39 |
| | EP | 323 | P | 5.11 | 0.38 |
| | EP | 323 | P | 6.20 | 0.39 |
| | EP | 319 | C | 5.11 | 0.36 |
| | EP | 308 | C | 4.70 | 0.54 |
| | EP | 302 | P | - | - |
| | EP | 301 | P | 5.50 | 0.36 |
| | EP | 296 | C | 4.95 | 0.47 |
| 7 | EP | 335 | P | 4.66 | 0.60 |
| | EP | 331 | P | 5.80 | 0.43 |
| | EP | 329 | C | 4.57 | 0.60 |
| | EP | 323 | C | 4.89 | 0.53 |

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a. Determined on May 4, 5, and 6, 1971. Estimated fly-ash concentration was 4.5 $gr/ft^3$ (standard conditions).

b. AH signifies a location ahead of the air heater, whereas EP signifies a location ahead of the precipitator.

c. C and P indicate cyclone and point-plane sampling probes, respectively.

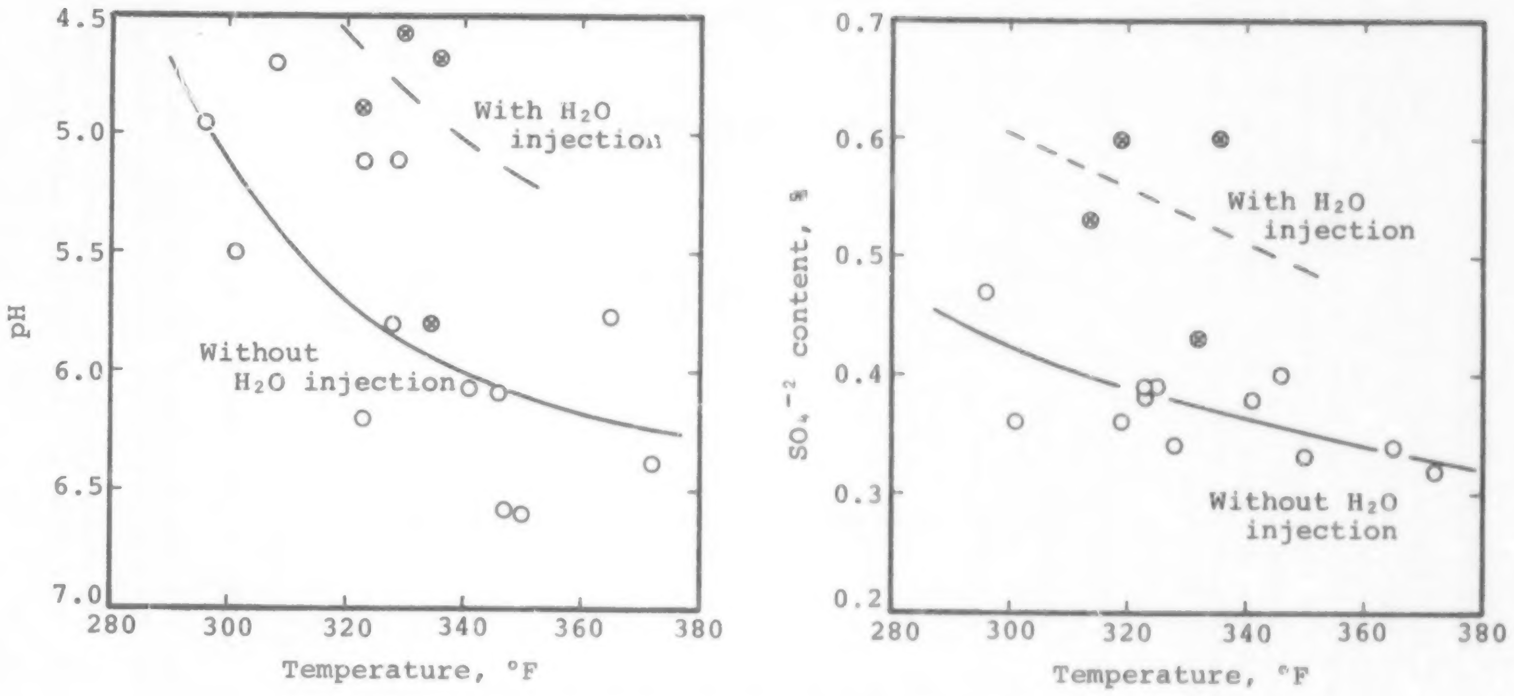

Figure 10. Sulfate Content and pH Value of Fly Ash at Kingston Unit 5 with and without $H_2O$ Injection

### d. Concentrations of flue gases

Table 33 lists the concentrations of $H_2O$, $SO_3$, and $SO_2$ found at Kingston Unit 5 with and without $H_2O$ injection. The observed concentrations of $H_2O$ and $SO_3$ are of primary interest. First, the observed concentrations of $H_2O$ show that the expected increase of about 7% increased during $H_2O$ injection. Second, the observed concentrations of $SO_3$ show wide variations with changes in temperature in the absence of $H_2O$ injection and with the change in $H_2O$ concentration during injection in the narrow temperature range between 320 and 330°F.

Table 33. Concentrations of Flue Gases at Kingston Unit 5[a]

| Sampling location[b] | Temp, °F | Calculated concn of injected $H_2O$, % | Concentrations of flue gases[c] | | |
|---|---|---|---|---|---|
| | | | $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm |
| AH | 645 | 0 | - | 13 | 1470 |
| | 640 | 0 | - | 14 | 1730 |
| | 640 | 0 | - | 11 | 1730 |
| | 635 | 0 | - | 13 | 1660 |
| | 635 | 0 | - | 9 | 1650 |
| EP | 365 | 0 | - | 15 | 1500 |
| | 363 | 0 | 5.7 | 18 | 1580 |
| | 345 | 0 | - | 10 | 1460 |
| | 341 | 0 | 6.9 | 16 | 1400 |
| | 324 | 0 | 7.5 | 10 | 1240 |
| | 324 | 0 | - | 9 | 1320 |
| | 319 | 0 | - | 9 | 1630 |
| | 319 | 0 | - | 12 | 1700 |
| | 314 | 0 | 5.9 | 9 | 1770 |
| | 296 | 0 | 6.2 | 5 | 1450 |
| | 296 | 0 | - | 4 | 1440 |
| EP | 334 | 7 | 13.6 | - | - |
| | 330 | 7 | - | 3 | 1300 |
| | 329 | 7 | - | 3 | 1410 |
| | 323 | 7 | 13.6 | 3 | 1410 |

---

a. Determined on May 4, 5, and 6, 1971.

b. AH signifies a location ahead of the air heater, whereas EP signifies a location ahead of the precipitator.

c. Expressed on the "wet" or actual basis. The concentration of $O_2$ recorded by the utility company was approximately 3%.

To show the variations in $SO_3$ concentration with temperature and $H_2O$ concentration, the observed $SO_3$ concentrations are plotted in Figure 11. From this figure, it is apparent that lowering the temperature from the values near 640°F ahead of the air heater to values near 360°F ahead of the precipitator caused an increase in the concentration of $SO_3$, which was probably the result of partial oxidation of the large excess of $SO_2$ by $O_2$; on the other hand, it is apparent that lowering the temperature from about 360 to 300°F ahead of the precipitator and increasing the collection of $SO_3$ by the fly ash (as observed) caused a sharp decrease in the concentration of $SO_3$. From the figure, it is to be noted, in conclusion that $H_2O$ injection lowered the $SO_3$ concentration appreciably at temperatures between 320 and 330°F. This concluding observation signifies that the conditioning of fly ash that occurs during $H_2O$ injection may be largely the result of increased collection of $SO_3$, rather than of $H_2O$.

## B. Gallatin Station, Unit 4

At Unit 4 of the Gallatin Station in the TVA system, the conditions of plant operation and the problems of precipitator operation are similar to those at the Widows Creek Station without $NH_3$ injection. Specifically, coal with a high sulfur content is burned, and the temperature within the precipitator is usually about 270°F—low enough to produce a fly-ash resistivity approaching the lower limit of acceptable values, where excessive reintrainment is to be expected.

Gallatin Unit 4 has a production capacity of about 330 MW, and it is operated with both a mechanical collector and an electrostatic precipitator for fly-ash removal. Unlike Widows Creek Unit 7, it does not have facilities for $NH_3$ injection.

A brief investigation was made of Gallatin Unit 4 on May 26 and 27, 1971. The experiments performed consisted only of determinations of the resistivity of the fly ash and chemical analysis of the fly ash. No effort was made to analyze coal samples or to determine flue-gas concentrations, because of the reported similarity of these parameters to those at Widows Creek Unit 7.

The results of the experiments are summarized in Table 34. The resistivity data show the expected trend of decreasing value with decreasing temperature and indicate the low value anticipated at the normal temperature of 270°F, about $1 \times 10^9$ ohm cm. The pH values do not show the expected trend toward lower values with decreasing temperatures, perhaps as a result of minor variations in coal composition during our studies; however, the $SO_4^{-2}$ data show the expected increases in total $SO_4^{-2}$ with decreases in temperature and also indicate that free $H_2SO_4$ represented a substantial function of the total $SO_4^{-2}$.

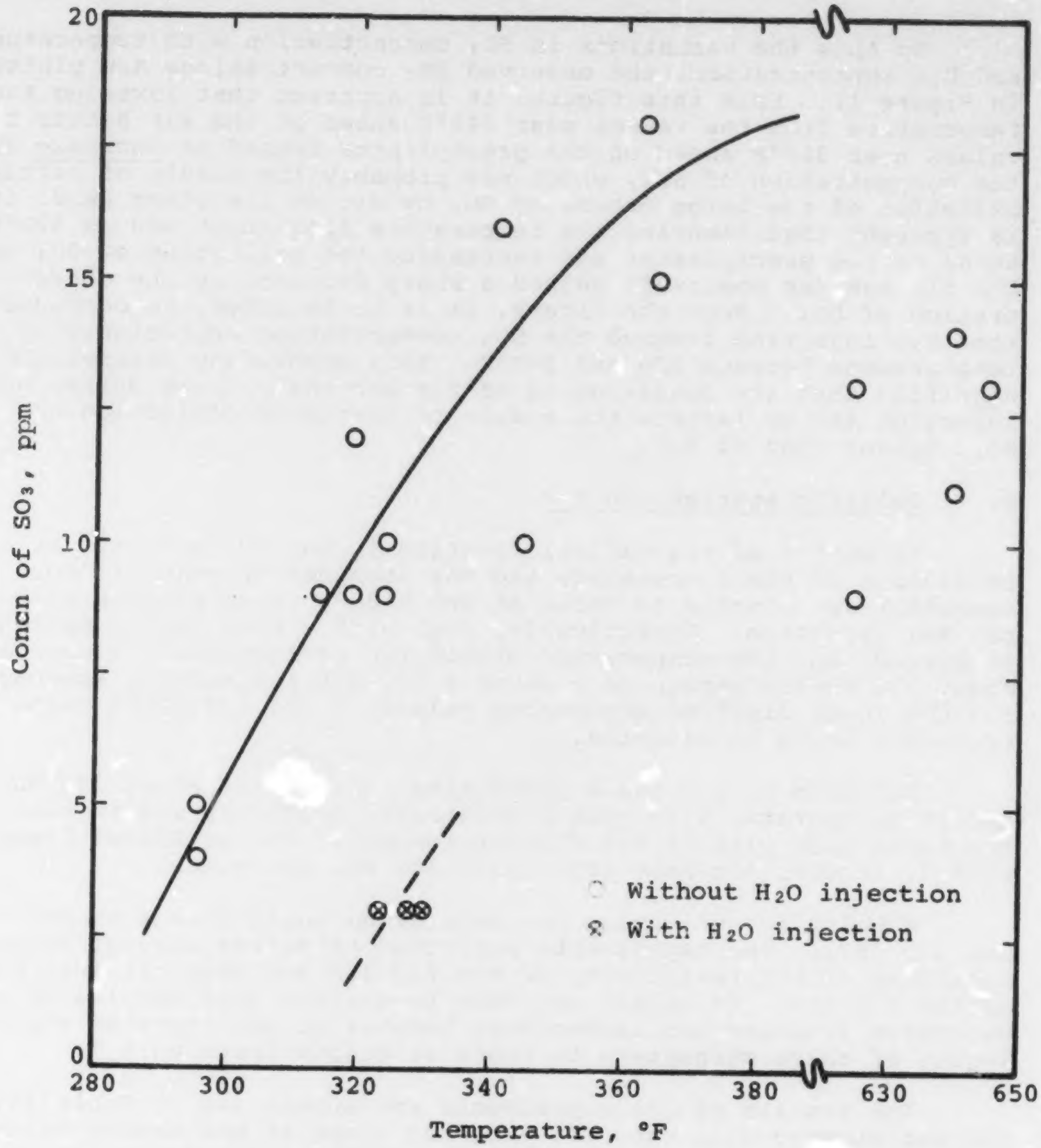

Figure 11. Concentrations of $SO_3$ at Kingston Unit 5

Table 34. Electrical Resistivity and Chemical Properties of Fly Ash at Gallatin Unit 4

| Temp, °F | Range of observed resistivity values, ohm cm[a] | Chemical properties pH | Soluble $SO_4^{-2}$, % Total | Soluble $SO_4^{-2}$, % $H_2SO_4$ |
|---|---|---|---|---|
| 329 | (2-3) x $10^{10}$ | 9.35 | 0.87 | 0.07 |
| 287 | (3-4) x $10^9$ | 9.80 | 1.15 | 0.09 |
| 260 | (2-6) x $10^8$ | 10.15 | 1.60 | 0.07 |

a. Determined on May 26 and 27, 1971, with the point-plane apparatus at an electric field of 2.5 kV/cm.

## C. Bull Run Station*

At the Bull Run Station in the TVA system, in contrast to Widows Creek and Gallatin Stations, coal of low sulfur content (about 1%) is normally used as the fuel. Thus, the fly ash at Bull Run should have a resistivity higher than that at Widows Creek or Gallatin, perhaps high enough not only to overcome the problem of reintrainment at either of those plants but to introduce the alternative problem of excessive sparking or back corona.

A brief study, comparable to that described in the preceding section for Gallatin Unit 4, was made at Bull Run Station on several dates in March, 1971, when two different coals were burned. The Bull Run Station is a 950-MW installation with only an electrostatic precipitator for collecting fly ash. Our work consisted only of determinations of fly-ash resistivity and chemical properties. Concentrations of $SO_2$ were determined by TVA personnel and found to be consistently in the range from 830 to 950 ppm, signifying that no appreciable difference existed in the sulfur content of the coal and that the percentage of sulfur was about 1%, the typical value.

The results of the fly-ash studies are given in Table 35. Resistivity values at a temperature of 270°F were, as expected, higher than those at the Widows Creek and Gallatin Stations, and high enough to lead to the usual problems in precipitator performance with high resistivity. The chemical analyses showed that the ash from one coal was acidic whereas the other was nearly neutral; in addition, these analyses showed lower concentrations of $SO_4^{-2}$ in the ash, as expected with the low concentrations of $SO_3$ predictable in flue gases from coal with only 1% sulfur.

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* Consists of only one large power-production unit.

Table 35. Electrical Resistivity and Chemical Properties of Fly Ash at Bull Run Station

| Coal[a] | Temp, °F | Range of observed resistivity values, ohm cm[b] | Chemical properties pH | $SO_4^{-2}$, % (total) |
|---|---|---|---|---|
| A | 270 | $(2\text{-}10) \times 10^{11}$ | 4.4 | 0.28 |
| B | 270 | $(2\text{-}10) \times 10^{11}$ | 6.0 | 0.35 |

---

a. The coals identified as A and B are referred to as "Haddox" and "Bull Run" coals, respectively.

b. Determined on May 16 and 23, 1971, with a cyclone probe at an electric field of 2.5 kV/cm.

## D. Z Station, Unit 1

Z Station cannot be identified by name, location, or owner. However, it is located in a region where coals of various compositions are available for use as fuel. On the basis of both analyses made in this laboratory and analyses reported by the Bureau of Mines,[31,32] sulfur contents of the coal can be expected to vary in the intermediate range of 1 to 2%.

Experiments were conducted during January, 1971, at Unit 1 of the Z Station, an installation designed with a 220-MW capacity and equipped with only an electrostatic precipitator for fly-ash removal. On two dates, January 6 and 7, the most extensive work was conducted and, thus, only the results obtained on these dates are given in this report. On these dates, percentages of sulfur in the coal were 0.95 and 1.90%, respectively, and the corresponding percentages of ash were 15.8 and 16.0%. The difference in sulfur concentrations on January 6 and 7 probably represent the extremes to be found in different coals burned from time to time during extended periods of plant operation.

Considerable difficulty was encountered in obtaining consistent values of resistivity in the range of temperatures investigated, 256 to 319°F. The results of the resistivity determinations, which are listed in Table 36, fail to show the expected upward trend with increasing temperature in the range studied. The data are, nevertheless, noteworthy in that they indicate that the resistivity was also higher than the maximum value of $2 \times 10^{10}$ ohm cm desired for efficient precipitator operation, notwithstanding the difference in $SO_3$ that should have been available for conditioning of the ash during combustion of the different coals. The results of the chemical analyses of the fly ash, which are included in Table 36, show that the ash was basic and contained only moderate amounts of $SO_4^{-2}$.

Table 36. Electrical Resistivity and Chemical Properties of Fly Ash at Z Station

| Date | Temp, °F | Resistivity,[a] ohm cm | Chemical properties | |
|---|---|---|---|---|
| | | | pH | $SO_4^{-2}$, % (total) |
| Jan. 6 | 256 | $3 \times 10^{12}$ | 10.7 | 0.41 |
| | 269 | $7 \times 10^{12}$ | - | - |
| | 283 | $3 \times 10^{12}$ | - | - |
| | 305 | $4 \times 10^{12}$ | - | - |
| | 319 | $1 \times 10^{13}$ | 10.9 | 0.32 |
| Jan. 7 | 269 | $1 \times 10^{12}$ | 9.7 | 0.45 |
| | 270 | $1 \times 10^{12}$ | - | - |
| | 278 | $1 \times 10^{12}$ | - | - |
| | 283 | $2 \times 10^{11}$ | 9.8 | 0.42 |
| | 287 | $7 \times 10^{11}$ | 9.8 | 0.41 |
| | 292 | $6 \times 10^{11}$ | - | - |
| | 296 | $3 \times 10^{11}$ | - | - |
| | 310 | $1 \times 10^{12}$ | 9.7 | 0.47 |

---

a. Determined with a cyclone probe at an electric field of 2.5 kV/cm.

The results of flue-gas analyses are given in Table 37. The maximum concentration of $SO_3$ that appeared to be available for conditioning of the fly ash was about 4 ppm, based on the analyses of samples taken ahead of the air heater on the date when the coal had the higher content of sulfur. This concentration seems surprisingly low in comparison with the concentration of about 20 ppm found at Kingston Unit 5 under similar conditions. One distinction in compositions of fly ash at the two plants—the higher basicity of the ash at the Z Station—may be the principal reason for the difference in observed $SO_3$ concentrations.

Table 37. Concentrations of Flue Gases at Z Station

| Date | Sampling location[a] | Temp, °F | Concentrations of flue gases[b] $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm |
|---|---|---|---|---|---|
| Jan. 6 | EP | 256 | 7.4 | 1 | 700 |
| | | 269 | - | 1 | 600 |
| Jan. 7 | AH | 600 | - | 4 | 820 |
| | | 600 | - | 5 | 860 |
| | EP | 292 | 6.9 | 1 | 910 |
| | | 300 | - | 2 | 1020 |

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a. AH signifies a location before the air heater, and EP signifies a location before the precipitator.

b. Expressed on the "wet" or actual basis.

## E. Shawnee Station, Unit 10

### 1. Description of the power unit

Unit 10 of the Shawnee Station in the TVA system was unique among the plants investigated during this program in that it was equipped with facilities to control the emission of $SO_2$ by injection of dry limestone into the boiler. Dry-limestone injection is one of several processes being evaluated for control of $SO_2$ emission; it is based on calcination of limestone ($CaCO_3$) in the boiler to produce lime (CaO) and on reaction of the CaO with $SO_2$ and $O_2$ in the flue gases to produce $CaSO_4$ on the surface of the CaO particles.[41] As reaction with the combination of $SO_2$ and $O_2$ occurs, simultaneous reactions of the CaO with $SO_2$ alone to produce $CaSO_3$ and with the small naturally occurring concentration of $SO_3$ to produce $CaSO_4$ may also occur.[42]

Our staff carried out studies at Shawnee during times of plant operation with and without $CaCO_3$ injection on July 15, 16, 21, and 22, 1971. Our principal objective in these studies was to determine the effect of CaO particles on the resistivity of the fly ash; however, we were also interested to learn the degree to which $CaCO_3$ would lower the concentration of $SO_2$ and $SO_3$. The studies were planned to include experiments when coals of different sulfur contents were used as fuels and thus a range of concentrations of $SO_2$ were subject to removal by reaction with CaO.

Shawnee Unit 10 has a production capacity of about 175 MW and produces flue gases at the rate of about 540,000 $ft^3$/min at 310°F and ambient pressure (about 315,000 $ft^3$/min under standard conditions). It is equipped with both a mechanical collector and an electrostatic precipitator to remove fly ash. It was investigated during $CaCO_3$ injection at rates of 167 and 333 lb/min; assuming complete calcination of the $CaCO_3$ occurred in the boiler, it thus produced CaO particulate concentrations of about 2.1 and 4.2 gr/$ft^3$, compared to estimated fly-ash concentrations in the range from 3.9 to 4.5 gr/$ft^3$ (standard conditions) with the ash percentage in the coal in the range from 16.3 to 19.5%.

## 2. Analyses of the coal and the limestone

The composition of the coal was deliberately varied during our field work at Shawnee Unit 10, especially with respect to the sulfur content. Compositions of coal samples collected at different times on different dates and analyzed in our laboratory are shown by the data in Table 38. The average daily percentage of sulfur ranged from 1.81 to 3.89%, and the percentage of ash ranged from 16.3 to 19.5%. On two days, especially July 21, the coal apparently varied in composition significantly when constant composition was desired.

Table 38. Sulfur and Ash Contents of Coal Burned at Shawnee Unit 10

| Date | Time of sampling | Concentration, % | |
|---|---|---|---|
| | | Sulfur | Ash |
| July 15 | Morning | 1.79 | 18.2 |
| | Midday | 1.78 | 18.1 |
| | Afternoon | 1.87 | 17.8 |
| | Average | 1.81 | 18.0 |
| July 16 | Morning | 3.82 | 16.1 |
| | Morning | 3.96 | 16.5 |
| | Average | 3.89 | 16.3 |
| July 21 | Morning | 3.71 | 22.0 |
| | Morning | 2.97 | 19.3 |
| | Midday | 2.54 | 17.3 |
| | Average | 3.07 | 19.5 |
| July 22 | Morning | 1.57 | 16.3 |
| | Midday | 1.96 | 17.4 |
| | Afternoon | 2.40 | 16.2 |
| | Average | 1.98 | 16.6 |

A sample of the $CaCO_3$ was analyzed for purity on the basis of the amount of HCl neutralized by a weighed sample. The apparent purity was about 98%, assuming that the impurities did not react as acid or base. The $CaCO_3$ injected in the boiler during all of our studies was described as a "coarse" grade, signifying that 50% of the particles by weight would pass a 400-mesh sieve (in contrast to a "fine" grade, of which 80% would pass a 400-mesh screen).

## 3. Results of experiments without limestone injection

### a. Resistivity of the fly ash

Each of the determinations of the resistivity of fly ash was made in a duct leading into the precipitator with the point-plane apparatus, operating with a wide range of electric fields in the collected sample. Because of the sampling requirements of another organization with the primary responsibility for operating and evaluating the $CaCO_3$ injection equipment, it was necessary in most of the experiments to determine resistivity in a high-temperature duct, where the range of observed temperatures was 330 to 417°F and thus well above the range at which electrostatic precipitators are normally operated. However, it was possible on one date to make the determinations at more appropriate temperatures in the range from 266 to 305°F.

The results of the determinations of resistivity without $CaCO_3$ injection are given in Table 39. In general, the data include values at electric fields ranging from 1 to 20 kV/cm. For some of the samples, however, data are omitted at several values of field, either because the range of fields used experimentally was restricted or because electrical breakdown occurred, as indicated for one sample at fields of 15 and 20 kV/cm.

The data in Table 39 will be discussed later in greater detail in a comparison with the data obtained when $CaCO_3$ was injected. One noteworthy feature of the data obtained, however, is the dependence of resistivity on electric field was diminished as the temperature increased. This finding—contrary to observations at Kingston Unit 5—may be illustrated by the data recorded for a temperature of 266°F and 305°F on July 16, for example, or more emphatically by the data at 266°F on July 16 and various temperatures up to 385°F on other dates, when the composition of the coal was different.

Table 39. Electrical Resistivity of Fly Ash at
Shawnee Unit 10 without Limestone Injection

| Date | Temp, °F | Resistivity, ohm cm, at various electric fields[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1.0 kV/cm | 2.5 kV/cm | 5.0 kV/cm | 10.0 kV/cm | 15.0 kV/cm | 20.0 kV/cm |
| July 15 | 375 | $2.3 \times 10^{10}$ | $1.4 \times 10^{10}$ | $8.0 \times 10^{9}$ | $5.0 \times 10^{9}$ | - | - |
| | 376 | - | - | $3.5 \times 10^{10}$ | $2.0 \times 10^{10}$ | $1.8 \times 10^{10}$ | $1.8 \times 10^{10}$ |
| July 16 | 266 | - | $8.0 \times 10^{10}$ | $3.5 \times 10^{10}$ | $1.2 \times 10^{8}$ | $6.0 \times 10^{7}$ | $5.0 \times 10^{7}$ |
| | 273 | - | - | $2.3 \times 10^{10}$ | $8.0 \times 10^{7}$ | - | - |
| | 305 | $7.0 \times 10^{10}$ | $4.0 \times 10^{10}$ | $1.8 \times 10^{10}$ | $1.0 \times 10^{10}$ | BD[b] | BD[b] |
| July 21 | 330 | $5.5 \times 10^{10}$ | $5.0 \times 10^{10}$ | $5.0 \times 10^{10}$ | $4.2 \times 10^{10}$ | $3.6 \times 10^{10}$ | - |
| July 22 | 375 | $5.8 \times 10^{10}$ | $5.0 \times 10^{10}$ | $4.0 \times 10^{10}$ | $3.0 \times 10^{10}$ | $2.5 \times 10^{10}$ | - |
| | 385 | $8.0 \times 10^{10}$ | $7.0 \times 10^{10}$ | $6.0 \times 10^{10}$ | $4.6 \times 10^{10}$ | $3.8 \times 10^{10}$ | $3.0 \times 10^{10}$ |

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a. Determined with a point-plane resistivity probe. No value is listed if the range of electric fields was not extended throughout the maximum range usually covered.

b. BD indicates that electrical breakdown occurred in the collected sample at the electric fields shown.

b. Chemical properties of the fly ash

Table 40 lists the observed values of chemical properties of fly-ash samples collected in the absence of $CaCO_3$ injection. This table includes the values of properties not generally determined in studies of plants other than Shawnee. It includes the total percentage of water-soluble material in each sample and the percentage of each sample dissolved as $Ca^{+2}$ ion. Determinations of these properties were made by comparing sample weights before and after extraction with water and by determining dissolved $Ca^{+2}$ by atomic absorption spectroscopy.

Table 40. Chemical Properties of Fly-Ash Samples Collected at Shawnee Unit 10 without Limestone Injection

| | | | Chemical properties of the fly ash[b] | | | |
|---|---|---|---|---|---|---|
| | | | | Water-soluble components, % | | |
| Date | Temp, °F | Concn of fly ash,[a] gr/ft³ | pH | Total | $SO_4^{-2}$ | $Ca^{+2}$ |
| July 15 | 375 | 4.2 | 10.2 | 6 | 1.7 | 1.0 |
| | 376 | 4.2 | 9.0 | 5 | 1.6 | 0.6 |
| July 16 | 266 | 3.9 | 6.2 | 6 | 1.1 | 0.4 |
| | 273 | 3.9 | 4.6 | 7 | 1.2 | 0.4 |
| | 305 | 3.9 | 4.2 | 2 | 1.4 | 0.4 |
| July 21 | 330 | 4.5 | 11.7 | 9 | 2.7[c] | –[c] |
| July 22 | 375 | 4.0 | 11.0 | 8 | 1.5 | 1.0 |
| | 385 | 4.0 | 11.0 | 8 | 1.5 | 0.8 |

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a. Estimated for standard conditions from the ash percentage in the coal.

b. All of the samples were collected in the point-plane resistivity probe.

c. Electron microprobe analyses for sulfur and calcium yielded percentage concentrations of 0.7% and 3.3%, respectively. The sulfur percentage is believed to be a reasonable value for the surface material; it is in reasonable agreement with the value of 0.9% calculated from the concentration of soluble $SO_4^{-2}$. However, the calcium percentage may include material below the surface (see Table 43).

The properties of the ash show significant variations with the different dates of collection, as expected from the differences in temperatures used for sampling and the differences in coal used as the fuel. The properties of the ash are discussed later in greater detail in comparison with the properties of ash found during $CaCO_3$ injection.

### c. Concentrations of flue gases

Concentrations of $H_2O$, $SO_3$, and $SO_2$ observed in the absence of $CaCO_3$ injection are listed in Table 41. The data for the sulfur oxides are of primary interest. They show, for example, the expected variations in the concentration of $SO_2$ as the result of variations in the sulfur content of the coal. They also show variations in the concentration of $SO_3$ as expected, in view of differences in coal and fly-ash compositions and differences in sampling temperatures.

Table 41. Concentrations of Flue Gases at Shawnee Unit 10 without Limestone Injection

| Date | Sampling location[a] | Temp, °F | Concentrations of flue gases[b] | | |
|---|---|---|---|---|---|
| | | | $H_2O$, % | $SO_3$, ppm | $SO_2$, ppm |
| July 15 | EP | 375 | 9.2 | 3 | 1580 |
| | EP | 376 | - | 5 | 1530 |
| July 16 | EP | 266 | 10.0 | 1 | 3030 |
| | EP | 305 | 9.4 | 5 | 2890 |
| | EP | 305 | - | 5 | 2880 |
| July 21 | AH | 750 | - | 1 | 2070 |
| | EP | 330 | 7.6 | <1 | 1740 |
| July 22 | AH | 720 | - | 1 | 1150 |

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a. AH signifies a location ahead of the air heater, and EP signifies a location ahead of the electrostatic precipitator.

b. Expressed on the "wet" actual basis. In the absence of a determination of the concentration of $H_2O$ on July 22, a value of 8% was assumed for calculating the concentrations of $SO_3$ and $SO_2$.

However, it is desirable to make certain observations about the variations in the concentration of $SO_3$, as follows:

- The data at temperatures above 350°F might be expected, on initial consideration, to show differences corresponding to differences in the sulfur percentage of the coal. However, they do not show the differences expected on this basis. The highest concentrations of $SO_3$ observed at temperatures above 350°F were found during combustion of the coal with the lowest percentage of sulfur (on July 15). The lack of correlation of observed $SO_3$ concentrations with percentages of sulfur in the coal must be a result of differences in the basicity of the ash and resulting differences in the extent of $SO_3$ collection by the ash. The highest concentrations of $SO_3$ above 350°F occurred in the presence of ash of relatively lower basicity and presumably low effectiveness for collecting $SO_3$.

- The data obtained at relatively low temperatures of 266 and 305°F on July 16, when the coal had the highest percentage of sulfur, indicate that significant losses of the available $SO_3$ occurred as a result of collection on the fly ash, especially at the lower of the two temperatures.

## 4. Results of experiments with limestone injection

### a. Resistivity of the dust

Table 42 lists the results of determinations of the resistivity of dust collected during periods of $CaCO_3$ injection. This dust consisted of mixtures of fly-ash and CaO particles, including the $SO_3$ and $SO_2$ collected as $CaSO_4$. One noteworthy feature of the data obtained at high temperatures is that the resistivity increased with increasing electric field, in distinction to the behavior of fly ash in previous studies with CaO particles absent.

Figure 12 compares the resistivity data obtained at a constant field, 5.0 kV/cm, with and without $CaCO_3$ injection throughout the study at Shawnee Unit 10. One graph is used to show all of the data obtained on different dates, despite differences in the properties of the coal and fly ash. The resistivity of the fly ash alone, as observed when $CaCO_3$ was not injected, is portrayed by one curve, whereas the resistivity of the fly ash-CaO mixtures, as produced when $CaCO_3$ was injected, is represented by another curve.

Table 42. Electrical Resistivity of Fly-Ash and CaO Particles at Shawnee Unit 10 during Limestone Injection

| Date | Reported injection rate of $CaCO_3$, lb/min | Temp, °F | Resistivity, ohm cm, at various electric fields[a] 1.0 kV/cm | 2.5 kV/cm | 5.0 kV/cm | 10.0 kV/cm | 15.0 kV/cm | 20.0 kV/cm |
|---|---|---|---|---|---|---|---|---|
| July 15 | 333 | 340 | - | - | $3.0 \times 10^{10}$ | $2.7 \times 10^{10}$ | - | - |
| July 16 | 333 | 255 | - | - | $4.0 \times 10^{11}$ | $2.4 \times 10^{11}$ | $1.5 \times 10^{11}$ | $9.0 \times 10^{10}$ |
| | 333 | 273 | - | - | $4.5 \times 10^{11}$ | $4.5 \times 10^{11}$ | $4.5 \times 10^{11}$ | $4.5 \times 10^{11}$ |
| July 21 | 167 | 407 | - | - | $1.3 \times 10^{13}$ | $1.7 \times 10^{13}$ | $2.3 \times 10^{13}$ | $2.6 \times 10^{13}$ |
| | 333 | 360 | - | - | $1.1 \times 10^{13}$ | $1.0 \times 10^{13}$ | $9.0 \times 10^{12}$ | $8.0 \times 10^{12}$ |
| July 27 | 333 | 417 | $4.0 \times 10^{11}$ | $5.0 \times 10^{11}$ | $8.0 \times 10^{11}$ | $1.2 \times 10^{12}$ | $1.6 \times 10^{12}$ | $2.0 \times 10^{12}$ |

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a. Determined with a point-plane resistivity probe. No value is listed if the range of electric fields was not extended throughout the maximum range usually covered.

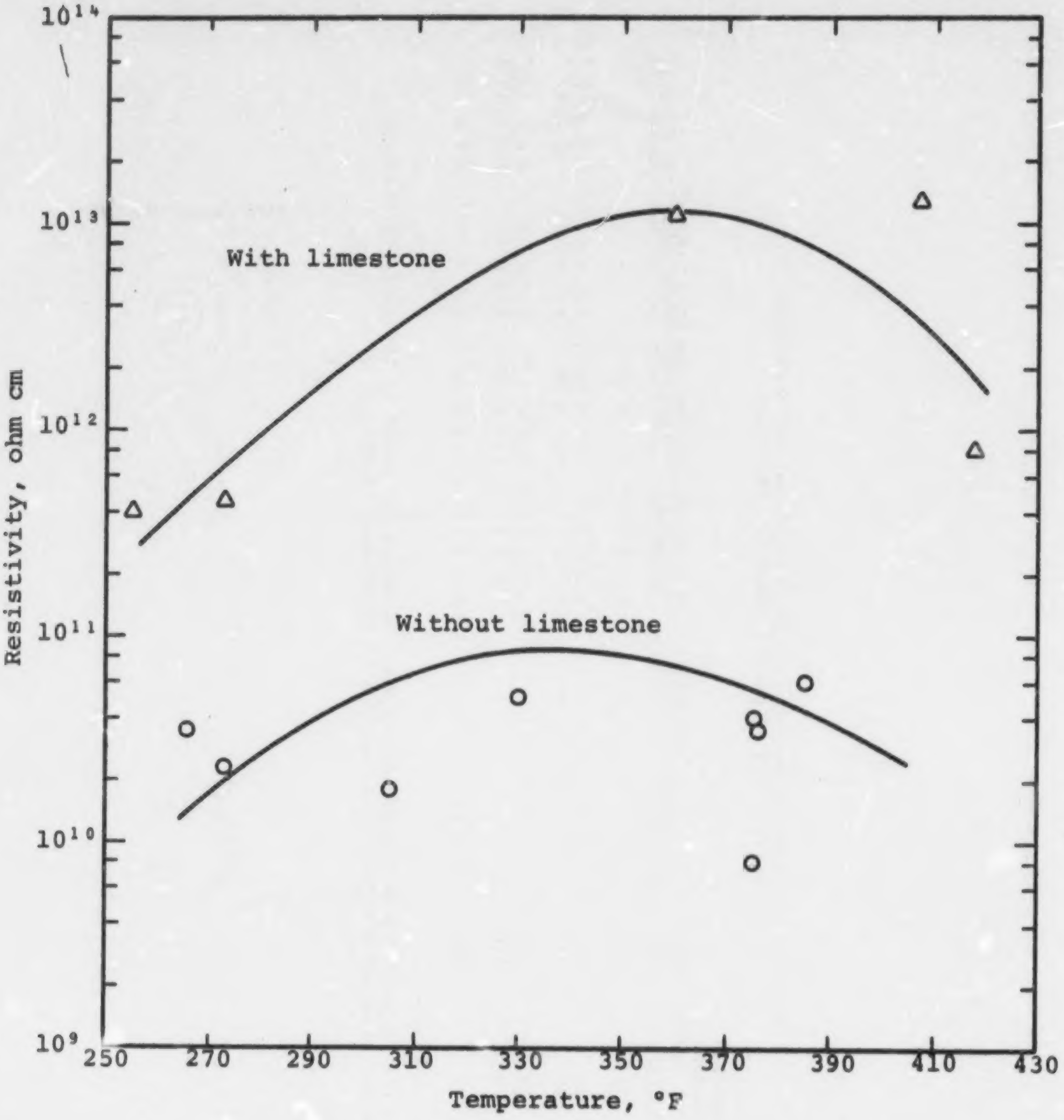

Figure 12. Resistivity of Fly Ash at Shawnee Unit 10 with and without Limestone Injection (Based on data in Tables 39 and 42 for an electric field of 5 kV/cm)

Figure 12 shows beyond reasonable doubt that injection of $CaCO_3$ raised the resistivity of collected dust by about two orders of magnitude. In the normal temperature range of precipitator operation, 275 to 325°F, the presence of CaO in the dust raised the resistivity to a range well above the acceptable upper limit of $2 \times 10^{10}$ ohm cm. As will be shown in the following section, the effect of CaO on resistivity occurred despite the presence of a large quantity of $SO_4^{-2}$ in the ash.

### b. Chemical properties of fly ash-CaO samples

Results of chemical studies of dust samples collected during times of $CaCO_3$ injection are listed in Table 43. Comparison of these results with the results of experiments without $CaCO_3$ injection (Table 40) leads to the following observations:

- The pH values of aqueous slurries of fly ash and CaO were uniformly high, ranging from 12.4 to 12.8 (compared with an observed value of 12.8 for an aqueous slurry of pure CaO), whereas the pH values of slurries of fly ash alone were consistently lower, ranging from a minimum of 4.2 to a maximum of 11.7.
- The percentages of water-soluble materials were consistently higher with CaO present, ranging from 22 to 48%. The corresponding percentages ranged from 2 to 8% with CaO absent. (Note: To facilitate dissolution of soluble materials, 0.1 g of each sample of particulate matter was first mixed with 30 ml of water to determine the pH value and then mixed with an additional 270 ml of water prior to determinations of the total amount of water-soluble components or of $SO_4^{-2}$ or $Ca^{+2}$.)
- The percentage of soluble $SO_4^{-2}$ increased markedly with CaO present. The minimum increase was 4.5% on July 21, and the maximum was 10.6% on July 16.
- The percentage of soluble $Ca^{+2}$ also increased markedly with CaO present, as expected. No comparison for July 21 is possible, but increases of about 4 to 9% occurred on the other dates.

### c. Concentrations of flue gases

Concentrations of flue gases found during periods of $CaCO_3$ injection are listed in Table 44. The principal observations to be made from these data are as follows:

Table 43. Chemical Properties of Samples of Fly Ash and CaO Collected at Shawnee Unit 10 during Limestone Injection

| Date | Limestone injection rate, lb/min | Temp, °F | Concn of particulate matter, gr/ft$^3$ [a] | | Chemical properties of the fly ash[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Water-soluble components, % | | |
| | | | Fly ash | CaO | pH | Total | $SO_4^{-2}$ (total) | $Ca^{+2}$ |
| July 15 | 333 | 340 | 4.2 | 4.2 | 12.4 | 31 | 6.2 | 6.0 |
| | 333 | 350 | 4.2 | 4.2 | 12.5 | 32 | 5.5 | 6.5 |
| July 16 | 333 | 255 | 3.9 | 4.2 | 12.7 | 48 | 11.7 | 9.2 |
| | 333 | 273 | 3.9 | 4.2 | 12.8 | 48 | 11.9 | 9.8 |
| July 21 | 167 | 407 | 4.5 | 2.1 | 12.4 | 23 | 7.2 | 4.4 |
| | 333 | 360 | 4.5 | 4.2 | 12.4 | 22 | –[c] | –[c] |
| July 22 | 333 | 417 | 4.0 | 4.2 | 12.4 | 34 | 6.1 | 5.9 |

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a. Expressed for standard conditions.

b. All of the samples were collected in the point-plane resistivity probe.

c. Electron microprobe analyses indicated that the percentages of sulfur and calcium were 3.3 and 31.2%, respectively. It is believed that a fairly reliable estimate of soluble $SO_4^{-2}$ (9.9%) can be made from the sulfur determination. However, it is obvious that an estimate of the soluble $Ca^{+2}$ cannot be made from the calcium determination, since the total percentage of soluble material was less than the percentage of calcium found. Evidently, the microprobe detected insoluble forms of calcium in the interior of the fly-ash particles.

Table 44. Concentrations of Flue Gases at Shawnee Unit 10 during Limestone Injection

| Date | Limestone injection<br>Rate, lb/min | <br>Mole ratio, $CaO:SO_2$[a] | Sampling location[b] | Temp, °F | Concentrations of flue gases[c]<br>$H_2O$, % | <br>$SO_3$, ppm | <br>$SO_2$, ppm |
|---|---|---|---|---|---|---|---|
| July 15 | 333 | 2.2 | EP | 400 | - | 1.2 | 962 |
| | 333 | 2.2 | EP | 340 | - | 1.1 | 962 |
| July 16 | 333 | 1.2 | AH | 765 | - | 1.0 | 1860 |
| July 21 | 167 | 0.9 | EP | 420 | 8.2 | 1.1 | 2072 |
| | 333 | 1.8 | AH | 750 | - | 0.9 | 1621 |
| July 22 | 333 | 3.0 | AH | 740 | - | 0.5 | 800 |

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a. Calculated from the rate of $CaCO_3$ injection and the rate of $SO_2$ production in the absence of $CaCO_3$ injection, based on the observed $SO_2$ concentration and the estimated total flow rate of flue gases, approximately 540,000 ft³/min at 310°F and 1 atm.

b. AH signifies a location ahead of the air heater, and EP signifies a location ahead of the electrostatic precipitator.

c. Expressed on the "wet" or actual basis. In the absence of a determination of $H_2O$, values listed in Table 41 were used for calculating the concentrations of $SO_3$ and $SO_2$.

- On three of the four days of experimental work, the concentration of $SO_2$ was lowered by $CaCO_3$ injection by approximately 30%. On July 21, however, no clearcut effect on the concentration of $SO_2$ was apparent at either of the two rates of $CaCO_3$ injection. On this date, furthermore, no clearcut effect was evident from the concentrations of $SO_2$ determined by an instrumental method used by the plant personnel. The apparent explanation for the apparent ineffectiveness of $CaCO_3$ on July 21 is that the composition of the coal varied throughout the day and thus the concentration of $SO_2$ produced in the boiler varied during the period of sampling.

- Under circumstances where the concentration of $SO_3$ was observed to be above 1 ppm in the absence of $CaCO_3$ injection, the concentration was lowered to about 1 ppm during injection.

- Even with excess amounts of CaO present, as indicated by calculated $CaO:SO_2$ mole ratios as high as 3.0, the removal of $SO_2$ was far from complete. On July 22, for example, when the $CaO:SO_2$ ratio was 3.0, somewhat less than 30% of the $SO_2$ was removed; on this occasion, therefore, only about 10% of the available CaO was used. It is to be expected that utilization of the CaO will be incomplete, because a $CaSO_4$ surface coating masks a substantial part of the CaO and prevents reaction in the contact time allowed.

# VII. DISCUSSION OF THE RESULTS OF THE CONDITIONING STUDIES

## A. Interpretation of Resistivity Data

To preface the following discussion of the results of the conditioning studies, the several difficulties encountered in making and interpreting *in situ* measurements of electrical resistivity must be recalled. These difficulties can be enumerated as follows: (1) the uncertainty in the significance of the decreasing resistivity values obtained with the cyclone resistivity probes at increasing times of measurement; (2) the lack of a consistent relationship between resistivity values and the different electric fields applied in the point-plane resistivity probe (usually resistivity decreased with increasing electric field but sometimes it increased; sometimes the dependence of resistivity on electric field appeared to vary with temperature and sometimes it did not); (3) the lack of a consistent relationship between the reported data for the same electric field in the cyclone and point-plane samples (usually the values obtained with the cyclone samples were higher but sometimes they were about the same as those obtained with the point-plane samples—or even lower than the latter).

To the difficulties listed above, there can be added the problem of knowing how an experimentally observed value of resistivity compares to the value that is significant in the precipitator. It has been recommended by one author that electrical resistivity always be measured at the electric field required for electrical breakdown in the sample.[1] It is reasonable to question this approach, however, in view of the variance to be expected in the required electric field as a result of a wide variance in (1) the compaction of the fly ash; (2) the extent of contamination of the ash with unburned, highly conductive carbon particles; (3) the composition and the resistivity of the ash;* or (4) the composition and the resistivity of the flue gases.

Even in the face of the experimental and theoretical uncertainties listed above, we believe that we are on fairly firm grounds in discussing the experimental results on the usual basis of average values obtained at the same electric field (usually

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* The resistivity may be low enough to make sparking through the gases rather than breakdown in the deposited ash the power-limiting factor in a precipitator.

2.5 kV/cm) in both cyclone and point-plane samples, with time-zero values selected from the time-dependent cyclone data. The validity of this basis for discussing the resistivity data is discussed in considerable detail in another report from this laboratory.[16] Because of circumstances beyond our control, however, we are unable to use this basis for the data obtained at Cherokee Unit 2, where carbon contamination led to breakdown at electric fields lower than 2.5 kV/cm, or at the X Station, where the electric field was unreported (in the absence of specific information, the assumption is made that the field was that required for breakdown, but this assumption cannot be used to estimate the field quantitatively for reasons listed above).

## B. Discussion of Conditioning by Injected $SO_3$ or $H_2SO_4$

### 1. General conclusions

#### a. Type of conditioning agent

This research program dealt with two sources of $SO_3$ and $H_2SO_4$ conditioning agents—(1) stabilized anhydrous $SO_3$ available from Allied Chemical Corporation under the trade name Sulfan and (2) concentrated aqueous $H_2SO_4$ (available from various commercial sources but consistently characterized in composition by either the density, 66°Bé, or the weight percentage of $H_2SO_4$, 93.2%). With respect to the conditions under which the concentrated aqueous acid was evaporated and injected, this program included work with two types of $H_2SO_4$ injection processes, which are referred to in this report as low- and high-temperature processes. The two types of $H_2SO_4$ injection processes are different not only on the basis of temperature but on the basis of the chemical form to which the acid is converted by evaporation for transport through the injection lines; in the low-temperature process the vapor is predominantly $H_2SO_4$, and in the high-temperature process it is predominantly $SO_3$.

The results of our investigation showed an apparent failure to achieve the desired conditioning in only one of the five plants equipped with $SO_3$ and $H_2SO_4$ injection systems. This failure occurred in an installation that has a high-temperature $H_2SO_4$ system (Cherokee Unit 3). The reason for the failure was not identified, although several attempts were made to explain the failure. Perhaps a faulty or unreliable injection system caused the acid to be injected in an inactive form such as a $H_2SO_4$-$H_2O$ mist, in view of the possible exposure of the $SO_3$-$H_2O$ vapor mixture in the injection lines to a duct temperature below the vapor dew point. Because of the limited scope of our studies of the high-temperature $H_2SO_4$ system at Cherokee Unit 3, our findings should not be construed as an indication that such a system is basically unworkable.

In general, our experimental findings lead to the fundamental conclusion that either an $SO_3$ or a $H_2SO_4$ injection system may be used to condition high-resistivity ash with roughly the same likelihood of success. Such findings are not surprising in view of the fact that injection of either $SO_3$ or $H_2SO_4$ will theoretically lead to existence of only one of the two substances, $H_2SO_4$, in the usual range of precipitator temperatures. The choice between an $SO_3$ or a $H_2SO_4$ system apparently should be based not on the predicted efficiency of conditioning but on other factors, such as costs or other factors as discussed later in Section VIII.

### b. Concentration of conditioning agent

The results of this investigation indicate that injection of either $SO_3$ or $H_2SO_4$ at a rate sufficient to produce a concentration between 5 and 20 ppm by volume in the flue gases will usually be adequate for conditioning fly ash from low-sulfur coal. This conclusion is based on studies with fly ash of various compositions in a wide range of temperatures.

The data from four plants showing resistivity as a function of the concentration of injected agent are plotted in Figure 13.* It appears that one curve is reasonably appropriate for showing the resistivity data obtained at three of the plants but that a distinctly different and lower curve is needed to represent the data at the fourth plant (Cherokee Unit 2).

No clearcut explanation can be offered for the lower curve showing the data at Cherokee Unit 2. At least a possible explanation is that the curve was located below the expected range because of the influence of an abnormal concentration of carbon particles in the ash. However, this explanation does not seem altogether plausible, for the influence of the carbon should have been strongest in the absence of conditioning agent; thus, if it were possible to correct the data for the effects of the carbon, the data would still be abnormally low with the conditioning agent present.

The apparent location of data points along one curve for the other three plants in the Arapahoe, X, and Y Stations may be somewhat fortuitous, in view of the differences in fly-ash

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* The data from a fifth plant, Cherokee Unit 3, are omitted because of the uncertainty that the reported concentrations of agent in this plant were actually reached.

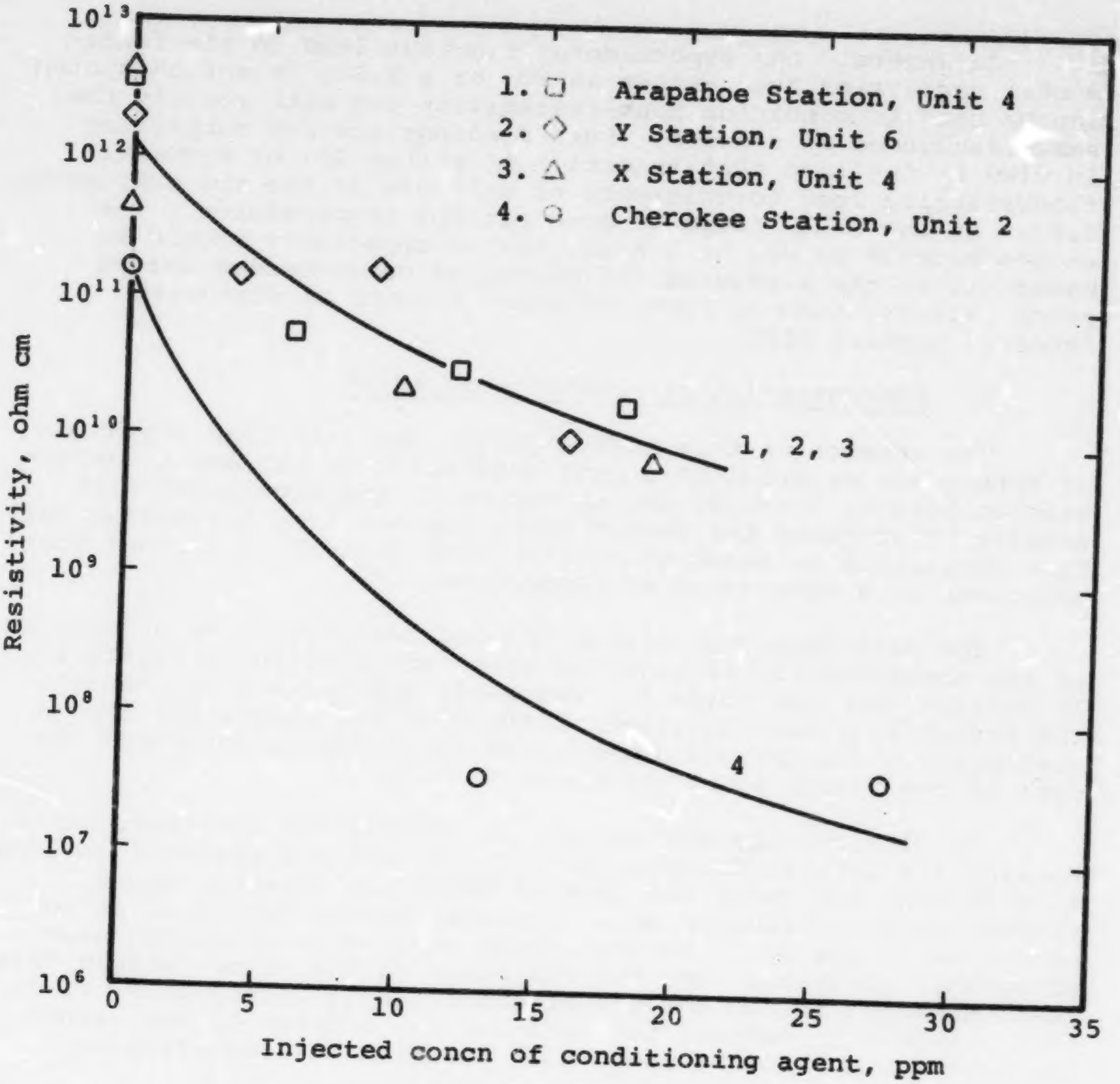

Figure 13. Resistivity of Fly Ash as a Function of the Injected Concentration of Conditioning Agent

composition, temperature, and other parameters. The data follow separate curves if plotted as functions of parameters other than the injected concentration of conditioning agent, as shown in the following sections.

It is worthy of emphasis that the concentration probably must, as a rule, be kept below some critical value, which is related to the capacity of the fly ash to collect the agent quantitatively. In two of the installations investigated, Unit 2 of the Cherokee Station and Unit 6 of the Y Station, the injection of excessive amounts of conditioning agent apparently led to stack emissions of unacceptably high $H_2SO_4$ concentrations.

### c. Location of the injection of conditioning agent

It is evident that $SO_3$ or $H_2SO_4$ can be used effectively if it is used to treat fly ash before or after partial removal of the ash occurs in a mechanical collector. Successful conditioning was observed in two plants without mechanical collectors (X and Y Stations) and in two plants with injection sites between mechanical and electrostatic collectors (Cherokee Unit 2 and Arapahoe Unit 4). Poor results were obtained in the one plant with injection ahead of both mechanical and electrostatic collectors (Cherokee Unit 3), but these results were evidently not characteristic of the results to be expected with dual collectors.

Observations made with different injection sites lead to the following conclusions:

- If fly ash is subjected to conditioning ahead of a mechanical collector, the large fraction of ash removed mechanically does not cause an unacceptable loss in the available concentration of conditioning agent. This conclusion is probably the result of the fact that the average size of particles collected mechanically is large compared with those at the entrance of the precipitator, thus the surface area to mass ratio is low. The total amount of the agent deposited on mechanically collected ash is therefore smaller than that deposited on ash entering the precipitator.

- If fly ash is in contact with the conditioning agent for only a brief time, as short as 1 sec in one plant investigated with injection immediately ahead of the electrostatic precipitator (the Y Station), an adequate degree of conditioning can still occur.

No work was done during this program with $SO_3$ or $H_2SO_4$ injection ahead of an air heater, although acid injection at this site has been reported.[9] Because of the thermodynamically predicted decomposition of $SO_3$ or $H_2SO_4$ to $SO_2$ and $O_2$ at the high temperatures that prevail in locations ahead of air heaters, as discussed later in Section VIII-C, injection at these locations appears unwise.

### d. Concentration and particle size of the fly ash

Information about the influence of concentration and particle size of fly ash on the effectiveness of conditioning was obtained during studies in plants supplied with coals of widely varying ash contents and operated with and without mechanical collectors.

Data showing resistivity as a function of the concentration of injected conditioning agent relative to fly-ash concentration and particle size are shown in Figures 14 and 15. In Figure 14, the concentration parameter is the ratio of the concentration of conditioning agent to the concentration of fly ash at the point of injection. In Figure 15, the concentration parameter is the ratio of the concentration of conditioning agent to the surface area of the fly ash (expressed in relative units) at the point of injection. The factor expressing surface area in relative units was calculated by multiplying the fly-ash concentration by the mean ratio of surface area to mass. The value of the area-to-mass ratio was calculated by the principles described by Irani and Callis,[43] with the use of particle-size distributions obtained on the number-median basis by microscopic counting. For fly ash that had not passed through a mechanical collector, the value of the area-to-mass ratio was proportional to the approximate factor 1/9.4, where 9.4 represents the pertinent particle size expressed in micrometers. For fly ash that had passed through a mechanical collector, the corresponding value of the area-to-mass ratio was proportional to the larger factor 1/2.9.

As plotted in Figure 14 or 15, the data for Cherokee Unit 2 do not show an unusual degree of divergence from the data for the other plants, in contrast to the behavior previously noted. In fact, the data for each plant appear to follow a distinct curve in Figure 14 or 15. Possible explanations for the different curves are offered in the following sections that discuss the influence of fly-ash composition and temperature.

### e. Composition of the fly ash

In connection with the influence of fly-ash composition, the conclusion of overriding importance is that no fly ash was found with a composition that prevented effective conditioning. Even so, with various compositions, it is to be expected that the concentration of conditioning agent required will vary significantly as a result of changes in fly-ash composition.

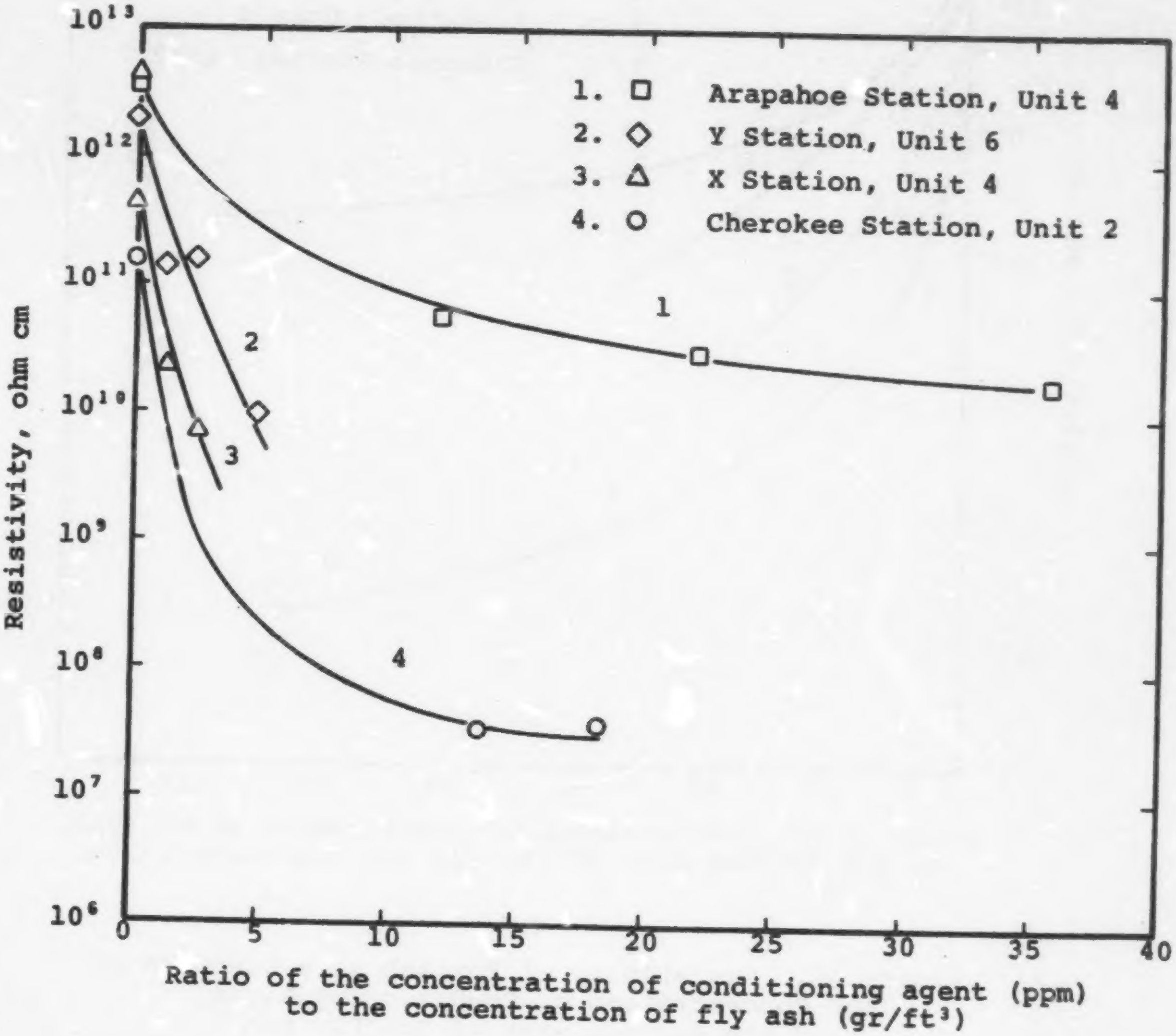

Figure 14. Resistivity of Fly Ash as a Function of the Relative Concentrations of Conditioning Agent and Fly Ash

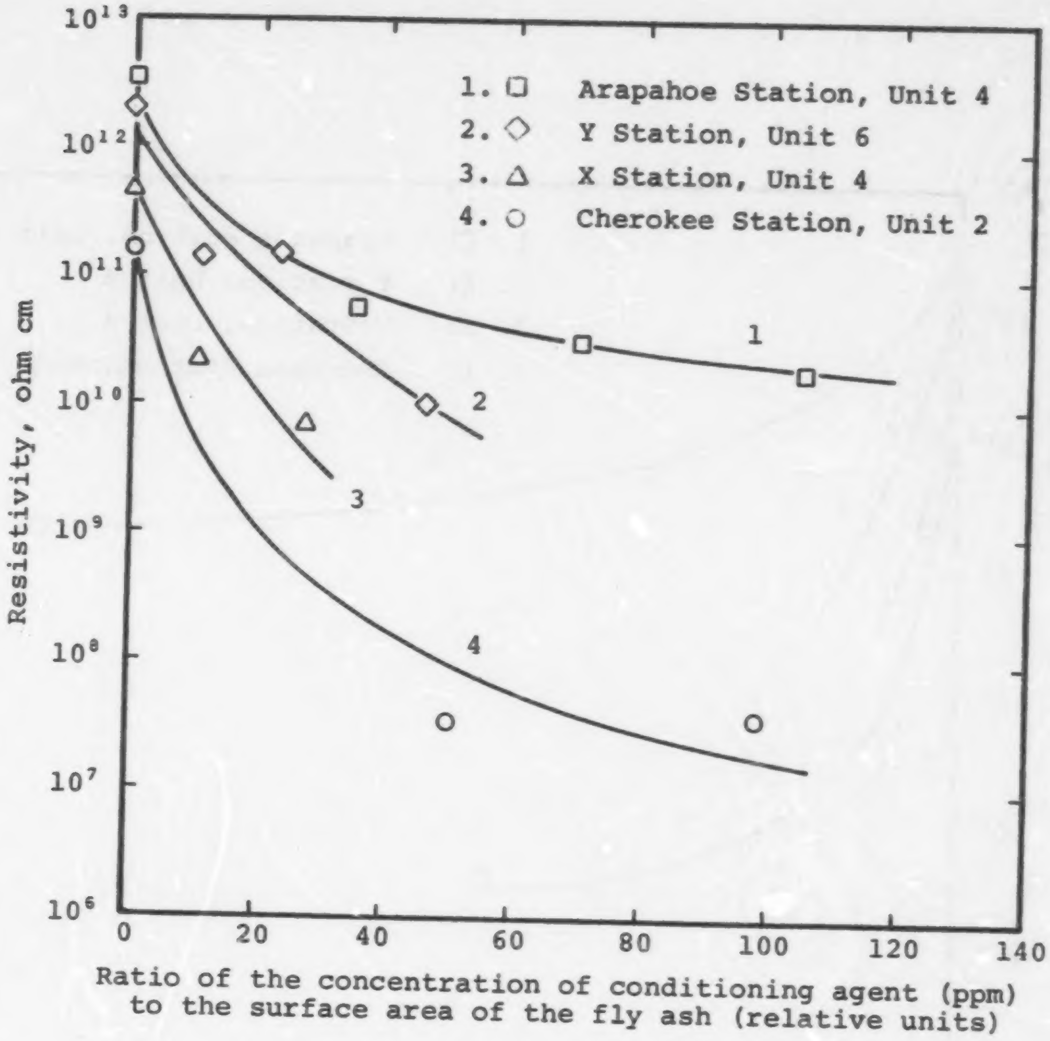

Figure 15. Resistivity of Fly Ash as a Function of the Concentration of Conditioning Agent and the Surface Area of the Fly ash

The unfavorable results reported for fly-ash conditioning at Unit 3 of the Cherokee Station might lead to the conclusion that fly ash produced from Routt County coal is difficult to condition. However, the quite favorable results reported for Unit 2 of this station with fly ash from the same coal show quite clearly that this conclusion would be distinctly erroneous. Moreover, as previously discussed, the reported concentrations of conditioning agent at Unit 3 are of doubtful validity.

The fact that fly-ash composition has a bearing on the effectiveness of conditioning is suggested by data shown previously in Figures 14 and 15, although the relative influences of composition and temperature cannot be clearly separated. However, consider as examples the data obtained at Cherokee Unit 2 and Arapahoe Unit 4 with fly ash of markedly different compositions but nearly equal temperatures (290 and 275°F, respectively). The Cherokee ash required much less conditioning agent than the Arapahoe ash on either basis shown in Figure 14 or 15, despite its somewhat higher temperature.

The importance of fly-ash composition is suggested further by the data plotted in Figure 16, in which resistivity is shown as a function of the $SO_4^{-2}$ content of the ash. If consideration is again given to the results at Cherokee Unit 2 and Arapahoe Unit 4, it is seen that the Cherokee ash required less gain in $SO_4^{-2}$ than the Arapahoe ash.

The difference in the behavior of the fly ash at the Cherokee and Araphaoe Stations may be attributed to the higher basicity of the Cherokee ash and the resulting requirement of more acidic conditioning agent for a given change in resistivity. Possible reasons for this phenomenon are discussed later in Section VII.B.2. Briefly stated, however, the reasons are that much of the conditioning agent is wasted in neutralizing basic components of the ash and that only a small part is used effectively to produce a surface layer of free acid.

### f. Temperature of the ash

The temperature of the fly ash during conditioning can be expected to influence the effectiveness of $SO_3$ or $H_2SO_4$ conditioning agent by exerting an influence on the adsorptivity of the ash for $H_2SO_4$ vapor or permitting the occurrence of acid condensation on fly-ash nuclei. It is difficult to separate the effects of temperature variations from the effects of composition changes in the different plants investigated. However, on the basis of recorded data and theoretical arguments given later in Section VII.B.2, we believe that it is reasonable to conclude that, in general, lowering the temperature will increase the effectiveness of conditioning. Lowering the temperature will increase the affinity of a neutral or weakly basic ash for $H_2SO_4$ vapor. Lowering the temperature will

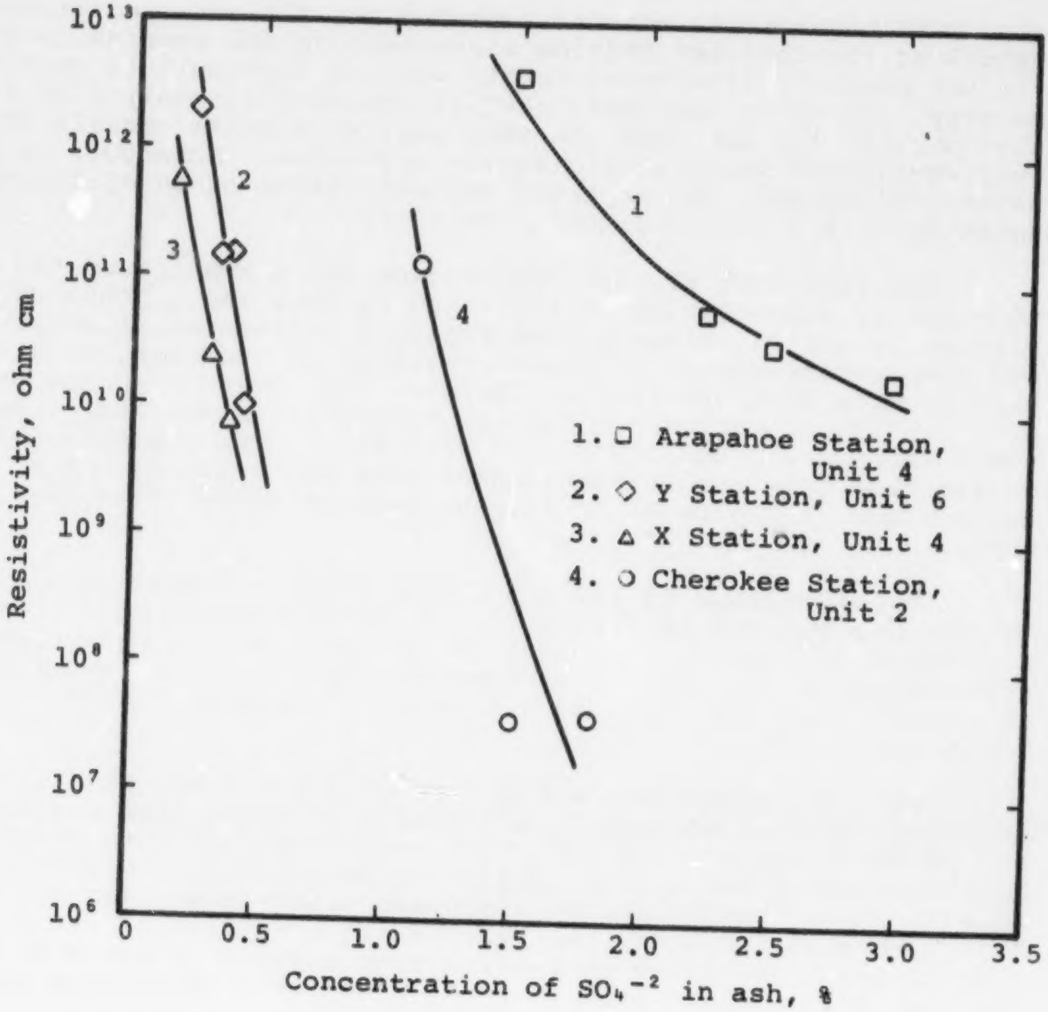

Figure 16. Resistivity of Fly Ash as a Function of the Sulfate Content of the Ash

probably have a smaller influence on the affinity of a strongly basic ash for $H_2SO_4$ but it will probably enhance the probability of formation of a free-acid layer by lowering the rate of acid-base reactions and minimizing the wastage of collected agent. If the temperature is lowered to such an extent that condensation of acid occurs on fly-ash nuclei, a very pronounced lowering of resistivity must be expected.

The above arguments may provide explanations for the behavior of the fly ash at the X Station, which appeared to be anomalous in several respects. This ash was comparable in basicity to the fly ash at the Arapahoe Station, but it appeared to be much more easily conditioned than the ash at Arapahoe and appeared to behave in a manner similar to the nearly neutral ash at the Y Station. The temperature in the X Station, 230°F, was below the acid dew point, whereas it was above the acid dew point in the other plants. Thus, the mechanism of acid collection may have been different at the X Station and the rate of reaction of collected acid with the fly ash was probably slower at this station.

## 2. Theoretical considerations

### a. Mechanisms of collection of $H_2SO_4$ on fly-ash particles

There are at least two distinctly different mechanisms by which $H_2SO_4$ in flue gas can be collected on the surfaces of fly-ash particles. One mechanism is the condensation of a mixture of $H_2SO_4$ and $H_2O$ vapors with fly-ash particles serving as condensation nuclei. This phenomenon results in the formation of a liquid layer on the particles; however, it can occur only if the temperature is below the dew point of the vapors existing in the duct. Other mechanisms involve the adsorption of $H_2SO_4$ and probably the concurrent adsorption of $H_2O$ as well. As discussed subsequently, different mechanisms of adsorption may exist, depending upon the sequence in which $H_2SO_4$ and $H_2O$ are adsorbed.

#### (1) Acid condensation

This phenomena of acid condensation can be critically analyzed only if reliable thermodynamic data exist for predicting dew points of $H_2SO_4$-$H_2O$ vapor mixtures or if reliable experimental data exist for showing dew points of adequately analyzed vapor mixtures.

Two notable attempts to secure the necessary thermodynamic data for predicting dew points have been made. The first of these two efforts was reported by Müller[44] in 1959 and was based on data previously compiled by Greenewalt[45] and Abel[46]; the second effort, reportedly with the advantage of more accurate background data, was reported by Gmitro and Vermeulen[47] in 1963 and summarized by Snowdon and Ryan[48] in 1969. Dew points predicted from the original work of Greenewalt and Abel and the later work of Gmitro and Vermeulen are shown in Figure 17 for various concentrations of $H_2SO_4$ at two different concentrations of $H_2O$, 7 and 10% (covering the usual range found in flue gases produced in coal-burning plants) for an assumed total pressure of 1 atm.* The curves in Figure 17 show that at a given set of $H_2SO_4$ and $H_2O$ concentrations the dew point predicted by the data of Greenewalt and Abel is approximately 30°F higher than the value predicted by the data of Gmitro and Vermeulen. They also show that at a given $H_2SO_4$ concentration the dew point predicted by either source of data decreases about 10°F as the concentration of $H_2O$ is lowered from 10 to 7%.

Numerous efforts have been made experimentally to determine dew points of $H_2SO_4$-$H_2O$ vapor mixtures of known composition. One of the most recent and perhaps most reliable study was reported by Lisle and Sensenbaugh.[24] The results of this study indicate that the dew point curves based on the work of Greenewalt and Abel are more accurate than those based on the work of Gmitro and Vermeulen, despite the access of the latter authors to more up-to-date reference data.

To predict the possibility that acid condensation may have occurred in the several plants where $SO_3$ and $H_2SO_4$ were injected as conditioning agents, the range of reported concentrations of the agent in each plant is shown by data points along a horizontal dashed line in Figure 17. The conclusion reached by comparing the locations of the several horizontal lines with the locations of the dew-point curves is that only the temperature at the X Station was clearly below the dew point at all injected concentrations of conditioning agent. The possibility that the temperature at Arapahoe Unit 4 was below the dew point at the two higher concentrations of conditioning agent cannot be excluded; however, the temperature was definitely above the dew point at the lowest concentration of the agent, which gave evidence of a marked reduction in resistivity. Finally, the possibility that the temperature in either of the other two plants

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* Recalculation of dewpoints from the data of Greenewalt and Abel was made, since the results of Müller's calculations from these data cannot be easily seen from Müller's graphical summary.

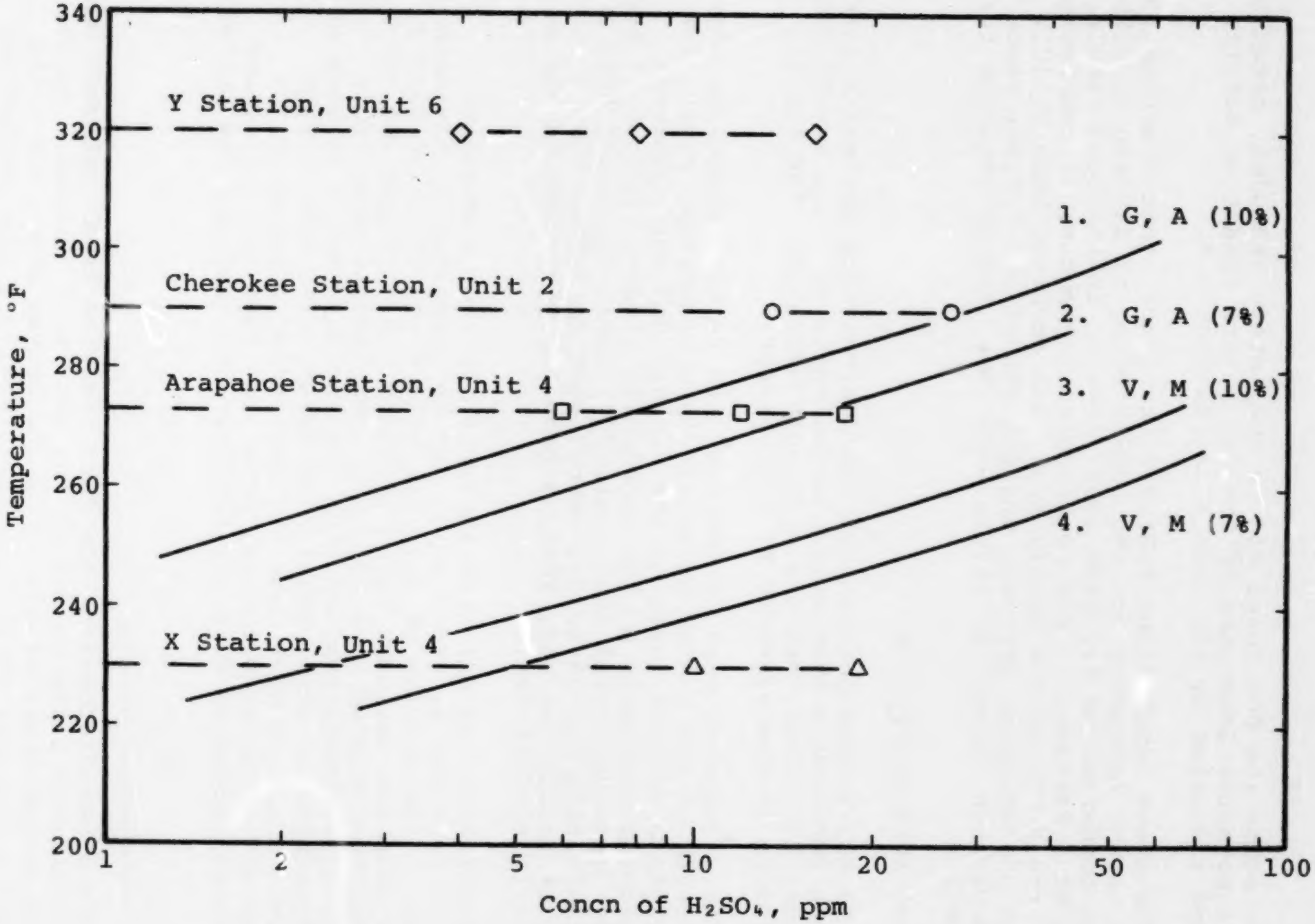

Figure 17. Dew Points Predicted from the Data of Greenewalt and Abel (G, A) and Gmitro and Vermeulen (V, M) for Flue Gases Containing $H_2SO_4$ at Various Concentrations in the Presence of $H_2O$ at Concentrations of 7 and 10%

was ever below the dew point can be completely excluded, assuming that the possible locations of the dew points cannot be outside the range indicated by the curves in the figure.*

The above conclusions indicate, at least, that condensation of acid is not necessary for the conditioning of fly ash by $H_2SO_4$. Although condensation may have been involved in the conditioning process at X Station, it did not necessarily occur; if chemisorption of the $H_2SO_4$ on the highly basic ash occurred more rapidly than the condensation process, the concentration of $H_2SO_4$ vapor could have been lowered to levels below the minimum required for condensation.

(2) Acid adsorption

The above consideration of the condensation mechanism leads us to the conclusion that acid adsorption is at least a sufficient mechanism, and, thus, not the necessary mechanism, for fly-ash conditioning in the presence of $H_2SO_4$ vapor.

The pioneering work by Chittum[7] led to the conclusion that conditioning of fly ash by an acidic vapor involves, first, the chemisorption of this vapor on the fly ash and then enhanced adsorption of $H_2O$ vapor on the chemically altered surface of the fly ash. Chittum argued that a strongly basic ash would have a greater affinity for an acidic vapor, such as $H_2SO_4$, than a neutral or acidic ash and, thus, a strongly basic ash should be most easily conditioned.

The results of our work appear to be inconsistent with Chittum's hypothesis. This point can be supported by the data obtained in the studies at Arapahoe Unit 4 and Cherokee Unit 2. The Arapahoe ash was more basic than the Cherokee ash and, moreover, was conditioned at a slightly lower temperature and a slightly lower concentration than the Cherokee ash. In view of the differences in the conditioning parameters, the Chittum hypothesis would predict more efficient conditioning of the Arapahoe ash. The experimental data show that more efficient conditioning occurred with the Cherokee ash, whether the criterion of effectiveness is based on the lowering of resistivity observed with a given rate of injection of conditioning agent or the lowering of resistivity observed with a given amount of agent collected as $SO_4^{-2}$ on the ash (Figures 13 and 16).

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* In the above discussion, the fact that the total pressure was not precisely 1 atm in all of the plants is ignored. In the Arapahoe and Cherokee plants in the Denver area, the total pressure was only about 0.83 atm. However, the conclusions reached above would not be significantly altered by making a correction for the difference in pressures.

Additional data contrary to the Chittum hypothesis were obtained at the Y Station, where the resistivity was lowered markedly with either a low rate of injection of conditioning agent or a small amount of agent collected on the ash, despite the near neutrality and high temperature of the unconditioned ash (two factors that were unfavorable for chemisorption).

Still other data contrary to the Chittum hypothesis were obtained at Shawnee Unit 10 with and without $CaCO_3$ injection in the boiler. With injection, the amount of $SO_3$ collected on the dust particles as $SO_4^{-2}$ was greatly increased, but the effectiveness of the $H_2O$ for conditioning the ash was markedly reduced.

It is our belief that a highly basic ash will require more acid conditioning agent than a neutral ash, in terms of either the concentration injected in the duct or the concentration collected in the ash, for the following reasons: (1) the acid initially collected is not simply adsorbed but it undergoes reaction with basic components of the ash, such as CaO, to form $SO_4^{-2}$ salts, such as $CaSO_4$, that may have little affinity for $H_2O$; (2) the amount of acid collected must increase to the point that an adequately thick protective layer of $SO_4^{-2}$ salts covers the remaining basic components of the ash and the amount of acid collected thereafter can exist on the surface of the ash in the form of $H_2SO_4$ rather than as $SO_4^{-2}$ salts; (3) the layer of $H_2SO_4$ ultimately produced exhibits a strong affinity for $H_2O$ and, thus, a layer consisting of both $H_2SO_4$ and $H_2O$ with the necessary electrical conductivity is finally produced on the surface of the ash.

The fact that only a small amount of collected $SO_4^{-2}$ was apparently required to condition the highly basic fly ash in the X Station appears, on initial consideration, to be inconsistent with the theoretical concepts outlined in the preceding paragraph. One possible rationale for the apparent discrepancy was that conditioning in the X Station occurred at an unusually low temperature, where the rate of diffusion of $H_2SO_4$ through the initially produced layer of $SO_4^{-2}$ salts would be relatively low and, thus, the required thickness of the protective layer of $SO_4^{-2}$ salts would be reduced.

### b. Mechanism of surface conduction on conditioned ash

It is our conviction that the predominant conductive material on conditioned fly ash is free $H_2SO_4$. At least semiquantative evidence for the presence of the acid has been repeatedly obtained during analyses of fly ash from various sources. Certainly the existence of $H_2SO_4$, probably in a mixture with $H_2O$, would provide a much higher conductivity than the existence of $H_2O$ alone, assuming that the behavior of the two substances in liquid form gives a reasonable basis for predicting their behavior in thin adsorbed layers on the surface of fly-ash particles.

## C. Discussion of Conditioning by Naturally Produced $SO_3$

As stated in Section I of this report, high resistivity of fly ash does not cause problems in the operation of electrostatic precipitators in power stations that burn coal with an adequate percentage of sulfur, in excess of 1% or perhaps even 2%. It is a matter of theoretical interest that if it were possible to maintain chemical equilibrium between the two products of sulfur combustion, $SO_2$ and $SO_3$, practically all of the $SO_2$ would be converted to $SO_3$ at temperatures below 1000°F with $O_2$ in the usual range of concentrations and, thus, even coal with a very low percentage of sulfur would produce an adequate concentration of $SO_3$.[49] It is a matter of record, however, that chemical equilibrium is not maintained, because $SO_2$ is always the predominant oxide of sulfur emitted from a coal-burning power station, as shown during this investigation and by other investigators.[27,28]

White[illegible] has indicated that, as a rule, about 1% of the sulfur oxides exists as $SO_3$ in the flue gases of a coal-burning power station. Other investigators[27] have reported that the percentage of $SO_3$ may be as high as 10%; our work has shown percentages usually below 1%, on the other hand. The fact that the percentage of $SO_3$ varies widely is not surprising. Although the gas-phase conversion of $SO_2$ to $SO_3$ is slow, comparatively rapid conversion may occur as the result of catalytic effects of various components of the fly ash and thus may lead to an unusually high percentage of $SO_3$. On the other hand, adsorption of the $SO_3$ on fly-ash particles may occur to an extensive degree and, thus, lead to an unusually low residual percentage of $SO_3$. Furthermore, it has been shown that variations in the amount of excess air supplied to the boiler can lead to significant changes in the concentration of $SO_3$.[50] In view of the varying data in the literature and the opposing phenomena that control the net conversion of $SO_2$ to $SO_3$, it is of interest to review the relative concentrations of $SO_2$ and $SO_3$ found in various power stations during this investigation and to determine what generalizations may be made about the adequacy of naturally produced $SO_3$ for conditioning fly ash.

The concentrations of $SO_2$ found in various power stations with various percentages of sulfur in the coal are plotted in Figure 18. With a few exceptions, the data indicate that the $SO_2$

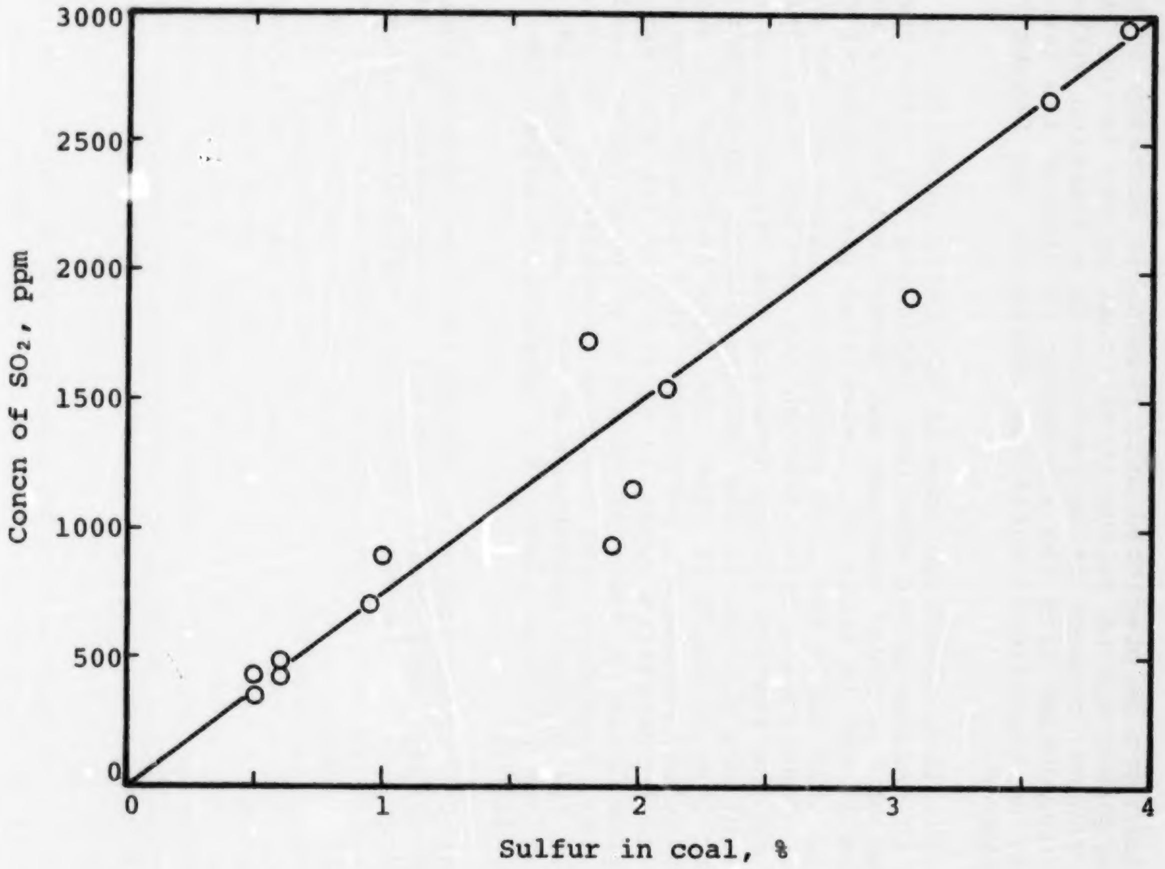

Figure 18. Concentration of $SO_2$ in Flue Gases as a Function of the Sulfur Percentage in Coal
(Each data point shows the $SO_2$ concentration in the middle of the observed range.)

concentration can be predicted with reasonable accuracy by multiplying the percentage of sulfur in the coal by the factor 750.* The predicted $SO_2$ concentration pertains to a location either upstream or downstream from the air heater in view of the fact that, in general, no significant variation across the air heater has been discovered.

The relative concentrations of naturally produced $SO_2$ and $SO_3$ found in various power stations, including the different concentrations of $SO_3$ found upstream and downstream from the air heater, are listed in Table 45. Calculated percentages of $SO_3$ are included in this table and also plotted in Figure 19. No attempt was made to construct a curve through the plotted data points, in view of both the scatter in the data and the variations in the properties of the fly ash in the various plants represented. Even so, from an overall point of view, the data in Figure 19 suggest that a peak value of the $SO_3$ percentage will usually occur within the range of temperatures normally existing in the air heater, with an upper limit of 600°F or more and a lower limit usually of 325°F or less, depending upon operating conditions. It is noteworthy that the highest percentage of $SO_3$ found, around 1%, occurred in the Kingston plant at a temperature within the range described, 365°F.

It is not unreasonable to assume that the maximum concentration of naturally produced $SO_3$ that will be effective for fly-ash conditioning will be the value found at a temperature around 350°F, where the peak in resistivity normally occurs as a result of the relative contributions of surface and volume conductivities. Higher concentrations may occur at higher temperatures, but part of the $SO_3$ that occurs at high temperatures may be collected by the fly ash as a low-conductivity $SO_4^{-2}$ salt when the temperature approaches the critical region around 350°F. Collection of the $SO_3$ remaining around 350°F, however, can lead to the formation of a high-conductivity acid layer, especially as the temperature approaches the usual range of precipitator operation of 325 to 275°F.

From the widely scattered data plotted in Figure 19, it is not possible to cite the percentage of sulfur oxides to be expected as $SO_3$ in all power plants at any given temperature. However, if it is assumed that the upper limit will, as a general rule, be around 0.7% in the critical region near 350°F—an

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* Some degree of variance is to be expected from variations in the excess air used for combustion and the heating value of the coal.

Table 45. Summary of Observed Concentrations of $SO_2$ and $SO_3$ in Power Plants Burning Coal of Various Sulfur Contents

| Power plant | Predicted concn of $SO_2$, ppm[a] | Observed concn range of $SO_2$, ppm | Observed concn of $SO_3$: Upstream from air heater: Temp, °F | Upstream: $SO_3$, ppm | Upstream: $SO_3$, %[b] | Downstream from air heater: Temp, °F | Downstream: $SO_3$, ppm | Downstream: $SO_3$, %[b] |
|---|---|---|---|---|---|---|---|---|
| Cherokee Unit 2 | 458 | 406-512 | 695 | 2 | 0.4 | 290 | 1-3 | 0.2-0.6 |
| Cherokee Unit 3 | 375 | 314-358 | 740 | <1 | <0.3 | 310 | 1 | 0.3 |
| Arapahoe Unit 4 | 367 | 387-446 | 740 | <1 | <0.3 | 275 | <1 | <0.3 |
| Y Station, Unit 6 | 465 | 373-488 | - | - | - | 320 | <1 | <0.3 |
| Widows Creek Unit 7 | 2690 | 2450-2860 | 625 | 15-20 | 0.6-0.8 | 285<br>255 | 15-18<br>8-10 | 0.6-0.7<br>0.3-0.4 |
| Kingston Unit 5 | 1590 | 1300-1770 | 640 | 9-13 | 0.6-0.9 | 365<br>325<br>295 | 15-18<br>9-10<br>4-5 | 0.9-1.2<br>0.6-0.7<br>0.3-0.4 |
| Z Station, Unit 1 | 712<br>1460 | 600-700<br>820-1020 | -<br>600 | -<br>4-5 | -<br>0.4-0.5 | 260<br>295 | 1<br>1-2 | 0.2<br>0.1-0.2 |
| Shawnee Unit 10 | 1360<br>2900 | 1530-1580<br>2880-3030 | -<br>- | -<br>- | -<br>- | 375<br>305 | 3-5<br>[illegible] | 0.2-0.3<br>0.2 |
|  | 2300<br>1480 | 1740-2070<br>1150 | 750<br>720 | 1<br>1 | 0.05<br>0.1 | 266<br>330<br>- | -<br><1<br>- | 0.04<br><0.05<br>- |

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a. Based on Figure 18, showing the concentration of $SO_2$ as a function of the sulfur percentage in coal.

b. Based on an $SO_2$ concentration at the middle of the observed range shown in the third column.

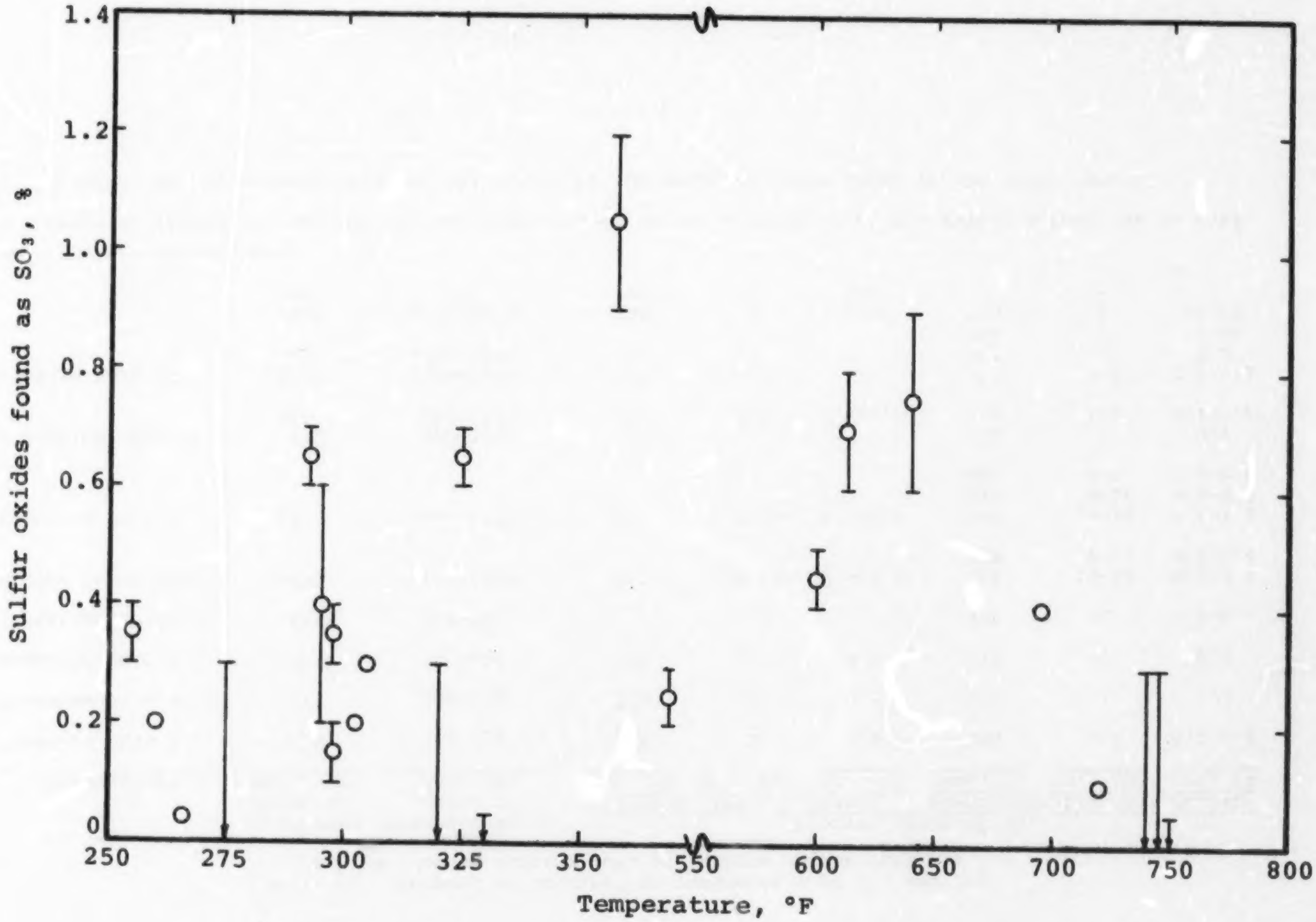

Figure 19. Percentage of Sulfur Oxides Found as $SO_3$ as a Function of Temperature in Various Plants

assumption reasonably consistent with the data plotted in Figure 19, despite some notable exceptions—calculations can be made of the minimum percentages of sulfur in coal that will produce various concentrations of $SO_3$ in the range up to 20 ppm, which appear adequate on the basis of studies with injected $SO_3$ or $H_2SO_4$. Calculations based on the relationship shown in Figure 18 between the $SO_2$ concentration in flue gases and the sulfur percentage in coal gave the following results:

| $SO_3$, ppm | Sulfur, % |
|---|---|
| 5 | 0.95 |
| 10 | 1.90 |
| 15 | 2.85 |
| 20 | 3.80 |

These calculations are generally consistent with industrial experience indicating that coal with a minimum sulfur percentage of 1 to 2% will be required if adequate conditioning of the fly ash by naturally produced $SO_3$ is to occur. They are also generally consistent with our resistivity data for fly ash that had been conditioned only with naturally occurring $SO_3$. Our data in this context may be summarized as follows:

- With coals containing around 0.5% of sulfur, the resistivity of the fly ash entering the precipitator was always excessive.
- With coals containing about 1% of sulfur, the resistivity of the fly ash was still above the maximum desired value.
- With coals containing about 2% of sulfur, the resistivity was slightly above or below the maximum desired value, depending upon the temperature.
- With coals containing 3% or more of sulfur, the resistivity was in the desired range or below this range, again depending upon the temperature.

## D. Discussion of Conditioning by Injected $H_2O$ or $NH_3$

Only a limited study of conditioning by injected $H_2O$ was included in this program. From the data obtained, it appears that a major effect of $H_2O$ is the more effective utilization of the $SO_3$ that is naturally produced. Certainly, at temperatures of 320 to 330°F, as studied at Kingston Unit 5, this effect is indicated by the experimental data. Perhaps at lower temperatures, which are more commonly found in electrostatic precipitators, the effect of $H_2O$ injection can be relatively independent of $SO_3$.

The relatively extensive study of $NH_3$ conditioning failed to explain the mechanism by which this agent overcomes the problem of low resistivity encountered with fly ash from high-sulfur coal. A major question not satisfactorily answered during this study is the fate of the injected $NH_3$. Thus, conclusions cannot be given in regard to possible mechanisms by which the $NH_3$ functions.

Conditioning of fly ash by $NH_3$ as a remedy for either low resistivity at the Widows Creek Station[11] or high resistivity at various Australian stations[9] is a subject to which intensive future research should be devoted.

# VIII. DISCUSSION OF BASIC THERMODYNAMIC, ENGINEERING, AND ECONOMIC ASPECTS OF CONDITIONING WITH $SO_3$ OR $H_2SO_4$

## A. Optional Processes for Generating Vapors of the Conditioning Agents

The various processes that can be used for injecting $SO_3$ or $H_2SO_4$ have been described by Whitehead.[6] They are as follows:

(1) Vaporization of stabilized $SO_3$

(2) Vaporization of $H_2SO_4$

(3) Stripping of $SO_3$ from oleum (a solution of $SO_3$ in anhydrous $H_2SO_4$)

(4) Catalytically converting part of the $SO_2$ in the flue gases to $SO_3$

(5) Burning sulfur and catalytically converting the $SO_2$ thus produced to $SO_3$.

Studies of the first two of the processes have been included during this investigation. The other three processes have various shortcomings that limit their applicability. Stripping $SO_3$ from oleum has the disadvantage that the residue of $H_2SO_4$ must be returned to the manufacturer for recharging with $SO_3$. Conversion of part of the $SO_2$ in the flue gases would require removal of the fly-ash particles from a stream of gases to avoid fouling of the $V_2O_5$ oxidation catalyst. Whitehead has estimated that in a plant burning coal with 0.4% sulfur the removal of fly-ash particles would require a hot-side precipitator capable of removing 99.9% of the fly ash in 8% of the total gas volume, and he has estimated further that the size of the precipitator would be about one-fifth of the size of the main precipitator.[6] Burning of sulfur suffers from the disadvantage of difficulties in controlling the burning process as required.

## B. Vaporization of Stabilized $SO_3$

### 1. Properties of $SO_3$

The commercial form of stabilized $SO_3$ that is available from Allied Chemical Corporation is described as a water-white liquid containing at least 99.5% of $SO_3$ by weight and minor amounts of $H_2SO_4$ and the stabilizing agent. Some of the physical properties of Sulfan reported by the manufacturer pertinent to its use as a conditioning agent are the following:

Specific gravity, 1.85 at 95°F
Viscosity, 1.5 cp at 90°F
1.3 cp at 100°F
Freezing point, 62.5°F
Boiling point, 113°F
Heat of vaporization, 230 Btu/lb

The fact that ambient temperature is frequently below the freezing point requires heating and insulation of storage and other handling facilities. A temperature range of 90 to 100°F is recommended during handling of the liquid.

The chemical properties of Sulfan require exceptional care in its handling. Liquid $SO_3$ and water react with explosive violence to produce $H_2SO_4$. Thus, when the $SO_3$ is evaporated in a stream of air, the air must be thoroughly dried; however, if commercial driers capable of lowering the water dew point to -40°F at pressures up to about 8 atm are used, the problem of drying the air can be satisfactorily overcome. Any liquid $SO_3$ spilled must be neutralized with soda ash (or some other suitable weak base) before it can be flushed away with water. Safety showers must be installed in the handling area for the protection of personnel.

The reactivity of liquid $SO_3$ also necessitates care in the selection of the materials used for storing and handling. For different components of the handling equipment, the following materials are recommended:

Storage tank—flange-quality steel (ASTM A285 Grade C), assembled in accordance with Part UW of ASME Code for Unfired Pressure Vessels.

Pipe and fittings—Schedule 80 black steel pipe with all-welded construction; stainless steel braided hose or reinforced Teflon hose for flexible assemblies

Valves and pumps—FA-20 alloy and Teflon components.

## 2. Processing equipment

A flow diagram showing the principal items of equipment needed in a system injecting evaporated $SO_3$ has been presented by Whitehead.[6] These items include the following:

- System for supplying air to the $SO_3$ evaporator
  - —compressor
  - —dryers
  - —heater

- Heated storage tank for $SO_3$
- Evaporator for $SO_3$, of the steam-heated vertical falling-film type (A surface area of 4 ft$^2$ is sufficient to vaporize $SO_3$ at the rate of 150 lb/hr and supply a 250-MW power unit with approximately 20 ppm of conditioning agent.)
- Heated lines leading from the evaporator to the injection manifold.

Although the equipment must be used with the indicated precautions, the injection of $SO_3$ offers some important process-engineering advantages over the injection of vapors from $H_2SO_4$. The higher volatility of $SO_3$ allows lower system operating temperatures and a higher ratio of $SO_3$ to carrier gas in the injection lines.

## C. Vaporization of $H_2SO_4$

### 1. Thermodynamic considerations

The thermodynamic aspects of the evaporation of concentrated aqueous $H_2SO_4$ at the usual commercial strength (66°Bé or 93.2% of $H_2SO_4$ by weight) are far more complex than those of the evaporation of $SO_3$, as a result of the fact that the $H_2SO_4$-$H_2O$ binary system departs markedly from ideal behavior at all relevant temperatures. The temperature and relative amounts of acid vapors and carrier gas used for the evaporation of $H_2SO_4$ must take into account the complex liquid-vapor equilibria in the binary $H_2SO_4$-$H_2O$ system that prevails at relatively low temperatures (up to about 400°F) and the additional complexities of vapor equilibria involving $H_2SO_4$, $SO_3$, $H_2O$, $SO_2$, and $O_2$ that occur at higher temperatures.

One of the types of $H_2SO_4$ evaporation and injection systems investigated during this program has been referred to as a "low-temperature" system. It is based on evaporation of the acid at temperatures of 400 to 500°F in air of ambient humidity levels. The maximum concentration of acid vapors that can be produced in this range of temperatures is limited by the low volatility of $H_2SO_4$ in the presence of $H_2O$ vapor at ambient concentrations, for which the value of 1% by volume may be used as a representative concentration (this value corresponds to a relative humidity of about 30% at 75°F). With the vapor-pressure data of Gmitro and Vermeulen,[47] calculations have been made of the maximum concentrations of acid vapors that are theoretically obtainable at temperatures of 400, 450, and 500°F in an injection system with optional total pressures of 1.0 atm and 2.0 atm. The results are listed in Table 46; they show that $H_2SO_4$ is sufficiently volatile to permit the injection lines to carry concentrations in the range from 12,000 to 146,000 ppm (1.2 to 14.6% by volume). In practice, however, a concentration much lower than the range theoretically obtainable—about 5,000 to 10,000 ppm—is maintained in the injection lines. Other data included in Table 46 are the calculated percentages of the total concentrations of $SO_3$ and $H_2SO_4$ that would be present as $SO_3$ under the conditions of evaporation described; these show that only 4 to 15% of the conditioning agent would be transported through the injection lines as $SO_3$, whereas 85 to 96% would be transported as $H_2SO_4$.

Table 46. Concentrations of Acid Vapors Theoretically Obtained from 66°Bé $H_2SO_4$ in a Low-Temperature Injection System

| Total pressure, atm | Temp, °F | Total concn of $SO_3$ and $H_2SO_4$, ppm | Percentage of total vapors present as $SO_3$ |
|---|---|---|---|
| 1.0 | 400 | 26,000 | 6 |
| | 450 | 66,000 | 10 |
| | 500 | 146,000 | 15 |
| 2.0 | 400 | 12,000 | 4 |
| | 450 | 32,000 | 9 |
| | 500 | 72,000 | 14 |

One practical reason for maintaining a concentration of only about 5000 ppm in the injection lines of the low-temperature $H_2SO_4$ system is that this concentration can be conveniently maintained with a co-current evaporator, in which 66°Bé $H_2SO_4$ is admitted at a temperature of about 75°F and preheated air is admitted at a temperature of about 490°F. We have estimated that the heat required to evaporate the acid and reach a final vapor temperature of about 450°F is approximately 590 Btu/lb. Air supplied at 490°F in sufficient quantity to produce a final temperature of 450°F will provide the heat required to produce a vapor concentration of 5000 ppm in the exit stream from the evaporator.

The second type of $H_2SO_4$ evaporation and injection system investigated during this program has been referred to as a "high-temperature" system. In the installation of this type at Cherokee Unit 3, the hot gases produced by burning natural gas are used to evaporate 66°Bé $H_2SO_4$ in the range of temperature from 700 to 1000°F. There is no problem in reaching very high vapor concentrations in this range, in view of the fact that the maximum boiling point of the $H_2SO_4$-$H_2O$ liquid system is exceeded.[47] It is of interest that in the range from 700 to 1000°F the vapor of

$H_2SO_4$ is almost completely dissociated as $SO_3$ and $H_2O$.[47] It must be kept in mind, however, that on injection through pipes that are not adequately insulated, the mixture of $SO_3$ and $H_2O$ may be cooled sufficiently to condense as an $H_2SO_4$-$H_2O$ liquid aerosol. The possibility of condensation in insufficiently insulated injection lines is enhanced by the high concentration of $H_2O$ vapor produced during the evaporation process.

Another interesting aspect of the high-temperature $H_2SO_4$ system is that partial decomposition of $SO_3$ to $SO_2$ and $O_2$ may occur if the concentration of $O_2$ is not maintained at a high level. Table 47 shows calculated values of the percentage of the $SO_3$ that may be converted to $SO_2$ at various assumed $O_2$ concentrations (the calculations were based on the data cited by Hedley[49]).

Table 47. Percentages of $SO_3$ Vapor Converted to $SO_2$ Vapor at Equilibrium at Various Temperatures and $O_2$ Concentrations in a High-Temperature Injection Process

| Temp, °F | Concn of $O_2$, % | | | | | |
|---|---|---|---|---|---|---|
| | 0.1 | 1.0 | 2.0 | 3.0 | 10.0 | 20.0 |
| 700 | 3 | 1 | 1 | 1 | 0 | 0 |
| 800 | 11 | 4 | 3 | 3 | 1 | 1 |
| 900 | 78 | 11 | 8 | 7 | 4 | 3 |
| 1000 | 53 | 26 | 20 | 17 | 10 | 7 |
| 1100 | 73 | 46 | 38 | 33 | 22 | 16 |
| 1200 | 86 | 66 | 58 | 53 | 38 | 30 |
| 1300 | 92 | 79 | 73 | 69 | 55 | 46 |
| 1400 | 96 | 88 | 84 | 81 | 70 | 62 |

### 2. Process-engineering considerations

The principal items of equipment now used in both low- and high-temperature $H_2SO_4$ injection systems are listed below:

Acid-storage tank

Metering pump

Acid vaporizer

Heat-traced ducts and injection manifolds.

In the high-temperature system, a low pressure blower producing an absolute pressure of about 1.1 atm (2 psig) is used to supply air for burning the natural gas and pumping the effluent vapors from the acid vaporizer to the injection ports. In the low-temperature system, a turbo-compressor is used to supply air at an absolute pressure of about 1.8 atm (12 psig) to an air heater and then to the acid vaporizer.

## D. Economic Aspects of $SO_3$ and $H_2SO_4$ Conditioning

### 1. Capital costs

Information secured from the Public Service Company of Colorado about the installed costs of various conditioning systems is summarized in Table 48. This information is for the conditioning systems now in use, which differ in some respects from those in use during our field studies at the Arapahoe and Cherokee Stations. The cost data differ substantially in several respects from the anticipated costs that were previously published in the literature.[30]

Table 48. Capital Costs of $SO_3$ and $H_2SO_4$ Conditioning Systems Installed for the Public Service Company of Colorado

| Type of System | Power units supplied | | Total power rating, MW, of units supplied | Approximate total cost, $ |
|---|---|---|---|---|
| | Number | Power rating, MW | | |
| $SO_3$ evaporation | 2 | 110 | | |
| | 1 | 360 | 580 | 500,000 |
| $H_2SO_4$ evaporation, high temperature | 1 | 165 | 165 | 300,000 |
| $H_2SO_4$ evaporation, low temperature | 2 | 44 | 198 | 400,000 |
| | 1 | 110 | | |
| $H_2SO_4$ evaporation, low temperature | 1 | 44 | 44 | 250,000 |

An independent estimate was made of the capital cost of an $SO_3$ conditioning system to supply a single 250-MW power plant, as shown in Table 49. The procedure used for estimating costs was based on ratios of total costs to direct equipment costs for process plants built in the last 15 years at an existing plant site.[51] Application of the same procedure to the $SO_3$ system installed to serve the multiple power units operated by the Public Service Company resulted in an estimate of about \$450,000—only 10% below the actual cost, showing the validity of estimation procedure.

Table 49. Estimate of Capital Cost of an $SO_3$ Injection System for a Single 250-MW Power Unit

| Item | Cost[a] | |
|---|---|---|
| Storage tank, horizontal, 10,000 gal | \$ 7,350 | |
| Custom-fabricated $SO_3$ evaporator, stainless steel, $\sim$4-ft$^2$ area | 12,000 | |
| Compressor, $\sim$100 ft$^3$/min (standard conditions), 125-psig delivery pressure (includes compressor, motor, air filter, after cooler, and receiver) | 14,000 | |
| Rotameters | 420 | |
| Metering pump | 940 | |
| Injection manifold | 2,000 | |
| Air heater | 600 | |
| Air dryer | 1,800 | |
| Steam boiler | 5,000 | |
| SUBTOTAL - equipment on the F.O.B. basis | \$ 44,000 | |
| Equipment freight cost, estimated as 5% of F.O.B. cost | 2,200 | |
| SUBTOTAL - equipment as delivered | \$ 46,200 | (E) |
| Installation cost, estimated as 47% of (E) | 21,700 | |
| Building, assumed to be 1000 ft$^2$ at \$20/ft$^2$ | 20,000 | |
| Piping, estimated as 66% of (E) | 30,500 | |
| Instrumentation, estimated as 18% of (E) | 8,300 | |
| Electrical auxiliaries, estimated as 11% of (E) | 5,100 | |
| SUBTOTAL, DIRECT COSTS | \$131,800 | (D) |
| Engineering & supervision costs, estimated as 33% of (E) | 15,200 | (I) |
| SUBTOTAL, DIRECT + INDIRECT COSTS | \$147,000 | (D,I) |
| Contractor's fee, estimated as 5% of (D,I) | 7,400 | |
| Contintency, estimated as 10% of (D,I) | 14,700 | |
| TOTAL | \$169,100 | |

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[a] Listed on the F.O.B. basis for each item of equipment on the first nine items.

The estimate given in Table 49 is considerably higher than recent estimates given in the literature. Darby and Heinrich[52] estimated the cost of an $SO_3$ injection system for a 300-MW plant to be about $63,000 in 1966, while Coutaller and Richard[53] gave an estimate for a 250-MW unit of $60,000 to $80,000 in 1967 (both of these estimates pertained to European installations). Actual experience of the Public Service Company and our independent estimate indicate that the literature estimates are unrealistically low for the installation of facilities in the United States under current economic conditions, certainly with the extent of instrumentation used in the Public Service Company plants.

An estimate of the cost of an $SO_3$ system to supply a single 500-MW power plant was made by use of the power rule, given by

$$C_n = C(R)^x$$

where $C_n$ and C are the capital costs for expanded and existing facilities, respectively; R is the ratio of expanded to existing capacity; and x is a size exponent, which has been found to range between 0.6 and 0.7 in many instances.[51] With an assumed value of 0.6 for the size exponent, the estimated cost for a 500-MW power unit is $256,000. It is assumed, on the other hand, that for a 125-MW unit, the cost would be the same as estimated for a 250-MW unit, because this cost ($169,000) appears to be about the minimum that can be reached in constructing an $SO_3$ injection facility. It is to be noted that the estimated cost of $256,000 to supply a single-unit 500-MW plant is much lower than the actual cost of $500,000 experienced by the Public Service Company in supplying a three-unit plant of only slight greater total capacity, 580 MW. The discrepancy in costs is the result of the multiplicity of facilities such as evaporators that must be provided in a system designed to supply two or more power units either concurrently or independently as the need arises.

Estimates of the costs of $H_2SO_4$ injection systems to supply individual power units of various sizes were based on the data supplied by the Public Service Company. For a high-temperature system supplying a 165-MW plant, the actual cost of $300,000 was used as the base figure. For a low-temperature $H_2SO_4$ system supplying a single 198-MW plant, it was assumed that the cost would be about $325,000* rather than the $400,000 spent to supply three units with the same total production capacity. For the two types of systems serving power units of 250- and 500-MW capacities, capital costs were calculated from the power rule. For a power plant of 125 MW, it was assumed that the cost of a high-temperature system would be \$300,000, the same as that experienced for a 165-MW plant. For a plant of the same capacity, the cost of a low-temperature system was estimated by averaging the actual cost of a 44-MW installation (\$250,000) with the estimated cost for a single-unit 198-MW plant (\$325,000), thus obtaining \$288,000.

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* This figure was reached arbitrarily by averaging the costs of facilities supplying three units of 198-MW total capacity and one unit of 44-MW capacity. The figure should clearly be less than that experienced for the 198-MW capacity, in view of the triplicate components needed to supply three units concurrently or independently.

The above-described estimates of capital costs of $SO_3$ and $H_2SO_4$ injection systems for single-unit 125-, 250-, and 500-MW power stations are summarized in Table 50.

Table 50. Estimates of Capital Costs of Conditioning Systems for Various Sizes of Single-Unit Power Stations

| Type of conditioning plant | Size of unit, MW | | |
|---|---|---|---|
| | 125 | 250 | 500 |
| Stabilized $SO_3$ evaporation | \$169,000 | \$169,000 | \$256,000 |
| High-temperature $H_2SO_4$ evaporation | 300,000 | 387,000 | 583,000 |
| Low-temperature $H_2SO_4$ evaporation | 288,000 | 375,000 | 570,000 |

### 2. Operating costs

A listing of energy and raw materials costs for three types of injection systems serving a single 250-MW power unit is given in Table 51. These costs are based on 7,000 operating hours at full load per year (load factor = 0.80). The following assumptions were used in obtaining the estimates.

- Liquid $SO_3$ cost = \$65/ton + \$21/ton shipping (400 miles)
- 66°Bé $H_2SO_4$ cost = \$31.60/ton + \$10/ton shipping (less than 200 miles)*
- Steam cost for $SO_3$ evaporation = \$1/1,000 lb

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* It is assumed that $H_2SO_4$ will, as a rule, be more accessible than $SO_3$.

Table 51. Itemized Energy and Raw Material Costs for Three Types of Acid Injection Systems for a Single 250-MW Power Unit

| Type of system | Item | Injected concn, 10 ppm |  | Injected concn, 20 ppm |  |
|---|---|---|---|---|---|
|  |  | $/Year | Mils/kWh | $/Year | Mils/kWh |
| $SO_3$ evaporation | $SO_3$ | 22,000 | 0.0126 | 44,000 | 0.0252 |
|  | Steam | 125 | 0.0001 | 250 | 0.0001 |
|  | Power: Trace heating | 110 | 0.0001 | 110 | 0.0001 |
|  | Air compression | 780 | 0.0004 | 780 | 0.0004 |
|  | Air heating | 1,100 | 0.0006 | 1,100 | 0.0006 |
|  | Total | 24,100 | 0.0138 | 46,200 | 0.0264 |
| $H_2SO_4$ evaporation, high temperature | $H_2SO_4$ | 12,900 | 0.0074 | 25,800 | 0.0147 |
|  | Natural gas | 1,100 | 0.0006 | 2,200 | 0.0013 |
|  | Power: Trace heating | 800 | 0.0005 | 800 | 0.0005 |
|  | Air blower | 200 | 0.0001 | 400 | 0.0002 |
|  | Total | 15,000 | 0.0086 | 29,200 | 0.0167 |
| $H_2SO_4$ evaporation, low temperature | $H_2SO_4$ | 12,900 | 0.0074 | 25,800 | 0.0147 |
|  | Power: Trace heating | 500 | 0.0003 | 500 | 0.0003 |
|  | Air compression | 2,350 | 0.0013 | 4,700 | 0.0027 |
|  | Air heating | 5,750 | 0.0033 | 11,500 | 0.0066 |
|  | Total | 21,500 | 0.0123 | 42,500 | 0.0243 |

- Natural gas cost = \$0.40/1,000 ft$^3$ (standard conditions)
- Low-pressure blower and turbo-compressor efficiency = 40%
- High-pressure compressor efficiency = 50%

Airflow was assumed to be held constant with the $SO_3$ evaporation system, but a variation in airflow proportional to changes in injection level was assumed for the acid evaporation processes. A low pressure blower (2 psig) provides the air used for combustion in the high-temperature evaporation system; the required flow rate of air was based on an assumed concentration of $SO_3$ of 15,000 to 16,000 ppm in the injection line. A turbo-blower (10-15 psig) was assumed to provide the air in the low-temperature system; the flow rate of air was based on an assumed concentration of 5,500 ppm in the injection line.

The cost calculations indicate that the low-temperature acid evaporation system has total energy and raw material costs approximately equal to those of the $SO_3$ evaporation system, but they show that the high-temperature acid evaporation system is considerably cheaper to operate because of lower air-compression requirements and the lower cost of natural gas as a heat source. Other system designs are possible, of course, such as an indirectly fired gas heater in a low-temperature acid evaporation system.

### 3. Total annual operating costs

Tables 52, 53, and 54 were prepared to provide a comparison of the total estimated annual costs of operating the three types of injection processes for power units of 125-, 250-, and 500-MW generating capacities. Annual capital charges were computed as 14.5% of the estimated capital costs in Table 51, and annual labor maintenance costs were estimated at 5% of the capital costs.[51] Comparisons of the three systems indicate that the two $H_2SO_4$ evaporation processes would require similar expenditures but that the $SO_3$ process would be considerably less expensive. The lower annual operating cost of the $SO_3$ system arises primarily from the lower capital investment required. If $H_2SO_4$ evaporation systems should be installed in greater numbers than they have been to date, the cost per installation could decline and become comparable to that of the $SO_3$ system.

In view of present-day requirements for reduced stack particulate emissions, the differences in costs of the three conditioning processes are not likely to be significant. Instead of cost, the reliability and past performance of a system offered by a given vendor should be the primary basis upon which a conditioning process is selected.

Table 52. Estimated Total Operating Costs of Acid Injection in a Single 125-MW Power Unit

| Type of system | Item | Injected concn 10 ppm | | Injected concn, 20 ppm | |
|---|---|---|---|---|---|
| | | $/Year | Mils/kWh | $/Year | Mils/kWh |
| $SO_3$ evaporation | $SO_3$ | 11,000 | 0.0126 | 22,000 | 0.0252 |
| | Steam | 60 | 0.0001 | 125 | 0.0001 |
| | Electricity | 1,000 | 0.0011 | 1,000 | 0.0011 |
| | Capital charges | 24,500 | 0.0280 | 24,500 | 0.0280 |
| | Labor and maintenance | 8,500 | 0.0097 | 8,500 | 0.0097 |
| | Total | 45,100 | 0.0515 | 56,100 | 0.0641 |
| $H_2SO_4$ evaporation, high temperature | $H_2SO_4$ | 6,450 | 0.0074 | 12,900 | 0.0147 |
| | Fuel | 550 | 0.0006 | 1,100 | 0.0013 |
| | Electricity | 900 | 0.0010 | 1,000 | 0.0011 |
| | Capital charges | 43,500 | 0.0497 | 43,500 | 0.0497 |
| | Labor and maintenance | 15,000 | 0.0172 | 15,000 | 0.0172 |
| | Total | 66,400 | 0.0759 | 73,500 | 0.0840 |
| $H_2SO_4$ evaporation, low temperature | $H_2SO_4$ | 6,450 | 0.0074 | 12,900 | 0.0147 |
| | Electricity | 4,600 | 0.0053 | 8,600 | 0.0098 |
| | Capital charges | 41,800 | 0.0478 | 41,800 | 0.0478 |
| | Labor and maintenance | 14,400 | 0.0165 | 14,400 | 0.0165 |
| | Total | 67,200 | 0.0770 | 77,700 | 0.0888 |

Table 53. Estimated Total Operating Costs of Acid Injection in a Single 250-MW Power Unit

| Type of system | Item | Injected concn, 10 ppm | | Injected concn, 20 ppm | |
|---|---|---|---|---|---|
| | | $/Year | Mils/kWh | $/Year | Mils/kWh |
| $SO_3$ evaporation | $SO_3$ | 22,000 | 0.0126 | 44,000 | 0.0252 |
| | Steam | 125 | 0.0001 | 250 | 0.0001 |
| | Electricity | 2,000 | 0.0011 | 2,000 | 0.0011 |
| | Capital charges | 24,500 | 0.0140 | 24,500 | 0.0140 |
| | Labor and maintenance | 8,500 | 0.0049 | 8,500 | 0.0049 |
| | Total | 57,100 | 0.0327 | 79,200 | 0.0453 |
| $H_2SO_4$ evaporation, high temperature | $H_2SO_4$ | 12,900 | 0.0074 | 25,800 | 0.0147 |
| | Fuel | 1,100 | 0.0006 | 2,200 | 0.0013 |
| | Electricity | 1,000 | 0.0006 | 1,200 | 0.0007 |
| | Capital charges | 56,100 | 0.0321 | 56,100 | 0.0321 |
| | Labor and maintenance | 19,400 | 0.0111 | 19,400 | 0.0111 |
| | Total | 90,500 | 0.0518 | 104,700 | 0.0599 |
| $H_2SO_4$ evaporation, low temperature | $H_2SO_4$ | 12,900 | 0.0074 | 25,800 | 0.0147 |
| | Electricity | 8,600 | 0.0049 | 16,700 | 0.0096 |
| | Capital charges | 54,400 | 0.0311 | 54,400 | 0.0311 |
| | Labor and maintenance | 18,800 | 0.0108 | 18,800 | 0.0108 |
| | Total | 94,700 | 0.0542 | 115,700 | 0.0662 |

Table 54. Estimated Total Operating Costs of Acid Injection in a Single 500-MW Power Unit

| Type of system | Item | Injected concn, 10 ppm |  | Injected concn, 20 ppm |  |
|---|---|---|---|---|---|
|  |  | $/Year | Mils/kWh | $/Year | Mils/kWh |
| $SO_3$ evaporation | $SO_3$ | 44,000 | 0.0126 | 88,000 | 0.0252 |
|  | Steam | 250 | 0.0001 | 500 | 0.0001 |
|  | Electricity | 3,800 | 0.0011 | 3,800 | 0.0011 |
|  | Capital charges | 37,100 | 0.0106 | 37,100 | 0.0106 |
|  | Labor and maintenance | 12,800 | 0.0037 | 12,800 | 0.0037 |
|  | Total | 98,000 | 0.0281 | 142,200 | 0.0407 |
| $H_2SO_4$ evaporation, high temperature | $H_2SO_4$ | 25,800 | 0.0074 | 51,600 | 0.0147 |
|  | Fuel | 2,200 | 0.0006 | 4,400 | 0.0013 |
|  | Electricity | 1,200 | 0.0003 | 1,600 | 0.0005 |
|  | Capital charges | 84,600 | 0.0242 | 84,600 | 0.0242 |
|  | Labor and maintenance | 29,200 | 0.0083 | 29,200 | 0.0083 |
|  | Total | 143,000 | 0.0408 | 171,400 | 0.0490 |
| $H_2SO_4$ evaporation, low temperature | $H_2SO_4$ | 25,800 | 0.0074 | 51,600 | 0.0147 |
|  | Electricity | 16,700 | 0.0048 | 32,900 | 0.0094 |
|  | Capital charges | 82,600 | 0.0236 | 82,600 | 0.0236 |
|  | Labor and maintenance | 28,500 | 0.0082 | 28,500 | 0.0082 |
|  | Total | 153,600 | 0.0440 | 195,600 | 0.0559 |

# IX. CONCLUSIONS AND RECOMMENDATIONS*

This investigation has shown conclusively that different systems for injecting $SO_3$ or $H_2SO_4$ vapor in the flue gases of a coal-burning power station provide an effective remedy for the high electrical resistivity of fly ash produced from low-sulfur coal basically without regard to such parameters as fly-ash composition, concentration, or particle size. If high resistivity is the major factor limiting the performance of an electrostatic precipitator in the usual range of operating temperatures, injection of $SO_3$ or $H_2SO_4$ should markedly improve the efficiency of the precipitator for removing fly ash from the flue gases.

In the area of economics, this investigation has produced estimates of the costs of operating $SO_3$ and $H_2SO_4$ injection systems. Depending upon the type of injection system selected and the concentration of conditioning agent needed, the estimated annual operating costs are in the range from 0.03 to 0.07 mils/kWh in a plant of representative capacity, 250 MW. These costs are to be compared with the current average cost of power production of about 5.0 mils/kWh on a national basis. Again depending upon the plant operating parameters for the alternative methods of alleviating the problem of high resistivity—(1) reduction in the temperature of precipitator operation and (2) installation of a hot-side precipitator (located ahead of the air heater)—the incremental annual costs are in the ranges of (1) 0.03 to 0.05 mils/kWh and (2) 0.07 to 0.09 mils/kWh, respectively,[16] in a 250-MW plant.

Further research needs to be done (1) to establish the effectiveness of $NH_3$ and related compounds, such as $(NH_4)_2SO_4$, for coping with the high-resistivity problem associated with low-sulfur coal or the low-resistivity problem encountered with high-sulfur coal, (2) to establish the mechanisms by which $NH_3$ and the related compounds behave as conditioning agents, (3) to estimate the costs to be incurred in the use of these agents, and (4) to keep abreast of new developments in the use of $SO_3$ and $H_2SO_4$ conditioning. Continued work on conditioning in these areas will probably be resumed during the latter part of 1972.

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* A more extended discussion of the technical conclusions from this investigation is given in the Summary of this report (pages xiii through xvii).

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Walter R. Dickson, Supervisor of the Analytical Services Section

John P. Gooch, Research Chemical Engineer

Steven L. Estes, Associate Chemist

David E. Crawford, Associate Chemist

Edward J. Muglach, Engineering Technician

Submitted by:

Edward B. Dismukes

Edward B. Dismukes, Head
Physical Chemistry Section

Approved by:

Sabert Oglesby, Jr., Director
Engineering Research

Birmingham, Alabama
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## REFERENCES

1. H. J. White, "Industrial Electrostatic Precipitation", Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1963, pp. 295-300.

2. Southern Research Institute, "A Manual of Electrostatic Precipitator Technology, Part I—Fundamentals and Part II—Application Areas", prepared for the National Air Pollution Control Administration under Contract CPA 22-69-73, August 25, 1970.

3. H. G. T. Busby and K. Darby, J. Inst. Fuel 36, 184 (1963).

4. D. T. Berube, "Low Temperature Solution to High Resistivity Ash Problems", Proceedings of the Electrostatic Precipitator Symposium, Birmingham, Alabama, February 23-25, 1971 (sponsored by the Division of Process Control Engineering, Air Pollution Control Office, Environmental Protection Agency).

5. R. G. Ramsdell, Jr., "High Temperature Solution" (paper presented in the symposium cited in Reference 4).

6. C. Whitehead, "Gas Conditioning" (paper presented in the symposium cited in Reference 4).

7. J. F. Chittum, unpublished work on fly-ash surface conditioning at Western Precipitation Company (1942-1945) (reviewed in Reference 1).

8. H. J. White, Air Repair 3 (11), 79 (1953).

9. K. S. Watson and K. J. Blecher, Air Water Pollut. Int. J. 10, 573 (1966).

10. W. A. Baxter, J. Air Pollut. Contr. Assoc. 18, 817 (1968).

11. J. T. Reese and J. Greco, J. Air Pollut. Contr. Assoc. 18, 523 (1968).

12. J. Dalmon and D. Tidy, "Effect of Ammonium Sulfate and Related Compounds on the Performance of an Experimental Electrostatic Precipitator", Laboratory Note RD/L/N 112/68, Central Electricity Research Laboratories (Great Britain).

13. G. F. Goodeve, A. S. Eastman, and A. Dooley, Trans. Faraday Soc. 30, 1127 (1934).

14. M. Bodenstein and M. Katayama, *Z. Electrochem*. *15*, 244 (1909).

15. L. Cohen and R. W. Dickinson, *J. Sci. Instrum*. *40*, 72 (1963).

16. Southern Research Institute, Final Report on Contract CPA 70-166 ("An Electrostatic Precipitator Performance Model") to Division of Control Systems, Office of Air Programs, Environmental Protection Agency (in preparation).

17. G. K. Lee, F. D. Friedrick, and E. R. Mitchell, *J. Inst. Fuel* *40*, 397-405 (1967).

18. J. S. Fritz and S. S. Yamamura, *Anal. Chem*. *27*, 1461 (1955).

19. R. S. Fielder and C. H. Morgan, *Anal. Chim. Acta* *23*, 538 (1960).

20. A. A. Berk and L. R. Burdick, "A Method of Test for $SO_2$ and $SO_3$ in Flue Gases", U. S. Bur. Mines, Rep. Invest. *1950*, No. 4618.

21. J. F. Smith, J. A. Hultz, and A. A. Orning, "Sampling and Analysis of Flue Gas for Oxides of Sulfur and Nitrogen", U. S. Bur. Mines, Rep. Invest. *1968*, No. 7108.

22. D. Flint, *J. Soc. Chem. Ind*. *67*, 2 (1948).

23. Shell Development Company, Emeryville Method Series 4516/59a, Emeryville, California (1959).

24. E. S. Lisle and J. D. Sensenbaugh, *Combustion* *36* (1), 12 (1965).

25. H. Goksoyer and K. Ross, *J. Inst. Fuel* *35*, 177 (1962).

26. H. N. S. Schafer, *Anal. Chem*. *39*, 1719 (1967).

27. S. T. Cuffe, R. W. Gerstle, A. A. Orning, and C. H. Schwartz, *J. Air Pollut. Contr. Assoc*. *14*, 353 (1964).

28. R. W. Gerstle, S. T. Cuffe, A. A. Orning, and C. H. Schwartz, *J. Air Pollut. Contr. Assoc*. *15*, 59 (1965).

29. J. Griswold, "Fuels, Combustion and Furnaces", McGraw-Hill Book Company, New York, 1946, pp. 105-110.

30. *Electrical World* *173* (26), 22 (1970).

31. F. E. Walker and F. E. Hartner, "Forms of Sulfur in U. S. Coals", U. S. Bur. Mines, Information Circular 8301, 1966.

32. W. A. Selvig and F. H. Gibson, "Analysis of Ash from U. S. Coals", U. S. Bur. Mines, Bulletin 567, 1956.

33. H. J. White, Air Repair 5 (1), 37 (1955).

34. IGCI/ABMA Joint Technical Committee Survey, "Criteria for the Application of Dust Collectors to Coal-Fired Boilers", April 1965.

35. W. W. Duecker and J. R. West, "The Manufacture of Sulfuric Acid", Reinhold Publishing Corp., New York, 1959, p. 397.

36. W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis", John Wiley and Sons, Inc., New York, 1953, pp. 860-865.

37. F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid", D. Van Nostrand Co., Inc., Princeton, New Jersey, 1958, pp. 225-226.

38. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes", Cincinnati, 1971.

39. "Standard Methods for the Examination of Water and Wastewater", American Public Health Association, New York, 1965, pp. 239-240.

40. I. M. Kolthoff and E. B. Sandell, "Textbook of Inorganic Analysis", The Macmillan Company, New York, 1948.

41. Tennessee Valley Authority, "Sulfur Oxide Removal from Power Plant Stack Gas—Sorption by Limestone or Lime Dry Process", prepared for the National Center for Air Pollution Control, 1968.

42. T. R. Ingraham and P. Marier, J. Air Pollut. Contr. Assoc. 21, 347 (1971).

43. R. R. Irani and C. F. Callis, "Particle Size:Measurement, Interpretation, and Application", John Wiley and Sons, Inc., New York, 1963, pp. 25-33.

44. P. Müller, Chem.-Ing.-Tech. 31, 345 (1959).

45. C. H. Greenewalt, Ind. Eng. Chem. 17, 522 (1925).

46. E. Abel, J. Phys. Chem. 50, 260 (1946).

47. J. J. Gmitro and T. Vermeulen, "Vapor-Liquid Equilibria for Aqueous Sulfuric Acid", University of California Radiation Laboratory Report 10886, Berkeley, California, June 24, 1963.

48. P. N. Snowdon and M. A. Ryan, J. Inst. Fuel 42, 188 (1969).

49. A. B. Hedley in "The Mechanism of Corrosion by Fuel Impurities" (H. R. Johnson and D. J. Littler, editors), Butterworths, London, 1963, p. 204.

50. J. W. Laxton and P. J. Jackson, J. Inst. Fuel 37, 12 (1964).

51. M. S. Peters and K. D. Timmerhaus, "Plant Design and Economics for Chemical Engineers", Second Edition, McGraw-Hill Book Co., New York, 1968.

52. K. Darby and D. O. Heinrich, Staub 26 (11), 12 (1966).

53. J. Coutaller and C. Richard, "Improvement of Electrostatic Precipitators", Pollution Atmospherique, January-March 1967.